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FINAL REPORT

ABSORPTION SPECTROMETER MODIFICATIONS

AND FLIGHT TESTING

CONTRACT NO. NAS 9 -7958

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MSC TECHNICAL MONITOR

PREPARED BY

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Section 1

1.1 INTRODUCTION

This report presents the results of further modifications and testing of the remote sensing absorption spectrometer. This work was performed under contract No. NAS 9-7958, and is an extension of a previous contract "Absorption Spectrometer Feasibility Study" NAS 9-7242. The primary objective of the work reported herein was to further evaluate the airborne absorption spectrometer with regard to its potential capabilities as a remote sensor of atmospheric gases from earth orbit altitudes.

1.2 CONTRACT REQUIREMENTS

The work required to be performed under the terms of the current contract may be summarized as follows:

(1) Measurements of atmospheric NO_2 and SO_2 over Los Angeles, California.
(2) Modification of NASA spectrometer to incorporate I_2 sensing in addition to NO_2 and SO_2.
(3) Laboratory measurements of basic instrument performance parameters.
(4) Flight testing as required to establish performance characteristics; specifically to determine validity of radiation model, to examine effects of aerosol backscatter, to measure repeatability, threshold sensitivity, vertical distribution of NO_2 and SO_2 and ambient variations of pollutant concentrations.
(5) Ground measurements of iodine emissions as required to establish the usefulness of the iodine channel.
(6) Design of a possible advanced spectrometer which incorporates improvements deemed desirable from findings of current and previous programs and which is suitable for operation in NASA MSC aircraft.
(7) Preparation of reports and documentations relating to (6) above.

1.3 SUMMARY

This report presents the results of all items of work listed under para 1.1 above with the exception of the Los Angeles measurements which were reported on previously [(1)].

Following the Los Angeles survey, the spectrometer was removed from the aircraft and the I_2 channel was incorporated. The instrument was extensively refurbished and re-aligned and all three modes of operation; NO_2, SO_2 and I_2 evaluated in the laboratory. The aircraft mounting fixture was also substantially rebuilt and an improved ground track camera and CCTV navigation system added. Following this activity, a NO_2/SO_2 survey was flown for NAPCA in Chattanooga, Tennessee. Apart from the pollution data gathered, very useful noise data were obtained for NO_2 and SO_2 wavelengths over a wide range of terrain materials. Typical noise levels measured were as follows:

(1) 20 ppm-meters for SO_2 over rock and tree covered terrain
(2) 15 ppm-meters for NO_2 over rock and tree covered terrain

Iodine flights over the coast of Maine immediately followed the Chattanooga survey. These flights established:

(1) The basic feasibility of I_2 detection from an aircraft
(2) The noise level of the I_2 channel is 10 ppm-meters over tree covered terrain and water.
(3) that significantly higher levels of I_2 occur in the atmosphere above the kelp-rich coastline than further inland.

Following the I_2 flights, airborne experiments were conducted in the Toronto area over Lake Ontario and 40 miles north of Toronto over Lake Simcoe. These included mass flow and "m" factor measurements of NO_2 plumes from lakeshore industries, vertical profiles of both SO_2 and NO_2 pollution layers and ground based monitoring of ambient variations in moving air for SO_2, NO_2 and I_2. The results of the NO_2 mass flow measurements showed very close agreement with ground truth measurements

in the case of the isolated Lakeview Generating Station and to agree within a factor of 3 of the ground truth measurements of a more difficult-to-measure lakeshore oil refinery. These results are considered very encouraging considering the variability of wind speed at the time. "Over and under" measurements of a NO_2 plume over Lake Ontario also showed "m" factor values which agree closely, with theoretical values. The vertical profiles on the other hand showed that very significant errors can result in the measurement of absolute levels of gases in the atmosphere because of changes in the spectral distribution of backscattered radiation.

Although this type of error does not appear to affect the accuracy of plume measurements significantly, it definitely limits the ability of the system to measure well-diffused gases in the atmosphere. The cause of the error has been shown to be due to inherent limitations in the remote sensor mechanization which renders it sensitive to changes in spectral gradient. The instrument configuration described in this report (Section 4) is designed to overcome or at least minimize this limitation and at the same time provide greatly enhanced sensitivity with much reduced space and weight requirements. A brief comparison of characteristics of this present instrument and the proposed new instrument is as follows:

Parameter		Present Design	New Design
Photon-Limited[1] noise level	SO_2	1690 ppb-M	320 ppb-M
	NO_2	185 ppb-M	150 ppb-M
	I_2	85 ppb-M	11 ppb-M
Minimum descernable[2] signal level	SO_2	20 ppm-M	
	NO_2	15 ppm-M	
	I_2	10 ppm-M	
Beamwidth (acceptance angle)		30 mR x 30 mR	1° x 1°
Volume		2,940 in^3	624 in^3
Weight		44 lb.	12 lb.
Power Consumption		5 watts	3 watts (SS detector)[3] 5 watts (PM detector)[3]

Notes:

(1) for spacecraft performance, using rough estimates of earth reflectance and backscatter dilution factors, signal to noise ratio = 1/1, and integration time = 1 second

(2) for aircraft performance, signal to ratio = 1/1 and integration time 1 second

(3) add 10 watts for lamp power during calibration cycle.

Details of a proposed experimental high altitude balloon flight are included. The purpose of this experiment is to test the ability of the correlation spectrometer to detect and measure atmospheric pollution from above the ozone layer. This will include measurements of radiation backscattered from the atmosphere at several wavelengths.

FIGURE 1.1

Section 2

EQUIPMENT CONFIGURATION & LABORATORY EVALUATION

2.1 CONFIGURATION

The original aircraft equipment configuration as used in the initial Feasibility Study, NASA 9-7242 was limited to the basic components of an SO_2 sensing system. For the first phase of the current contract, that is the Los Angeles survey, the following modifications were effected:

(1) NO_2 mode added.

(2) Metrawatt recorder replaced by Brush oscillograph Model 16-2300.

(3) Pentax UV cameras replaced by Schackman Auto-camera MK III.

Subsequent to the Los Angeles work the following additional changes were made:

(4) I_2 mode added.

(5) Filter & correlation mask mounts re-designed to facilitate conversion from one mode to another.

(6) Photo-multiplier power supply (Venus type) replaced with high-speed BRL design.

(7) Aircraft mounting fixture re-built to reduce mechanical vibration and spurious light reflections and to accomodate additional ancillary equipment.

(8) Schackman camera replaced with Dehavilland MK VII and BRL intervalometer

(9) Company-funded Bollay Temp sensor Model 701 and pressure sensor Model 9100 plus leased C.C.T.V. system (Cohu 2000 series) added.

(10) Side looking window added to starboard pod.

Figure 1.1 shows the Aero Commander 500A in flight and Figure 1.2 illustrates the final equipment configuration.

2.2 SPECTROMETER MODIFICATIONS AND LABORATORY TESTS

Modifying the spectrometer to accomodate the NO_2 mode involved the installation of a grating-adjustment mechanism, the fabrication of a NO_2 reference cell and exit mask and re-design of the mask mounting arrangement. For the I_2 mode, only a new reference cell and mask were required. Figure 2-1 shows the spectrometer sensing head with the areas of modifications annotated. Figure 2.2 and 2.3 show NO_2 and SO_2 reference cells and mask/filter assemblies. The I_2 reference cell differed in that a fine nichrome heating wire was wound around the quartz walls of the cell and terminals provided for connection to a supply voltage. As shown in Figure 2.1 the grating adjustment mechanism was fitted with a 4-digit counter. The counter readout is related to the center wavelength of the spectral bandwidth in accordance with Figure 2.4. The shaded area represents the spectral bandwidth utilized at the exit mask.

Figure 2.5 shows the familiar SO_2 absorption spectra (at 5Å resolution) and two filter characteristics; the Ni SO_4 $6H_2O$ crystal + Corning CS7-54 combination used for all SO_2 data presented herein and an experimental interference filter only recently procured. Initial tests using the interference filter indicate an improvement in sensitivity of a factor of 2 to 3 is realizable but further investigation is required.

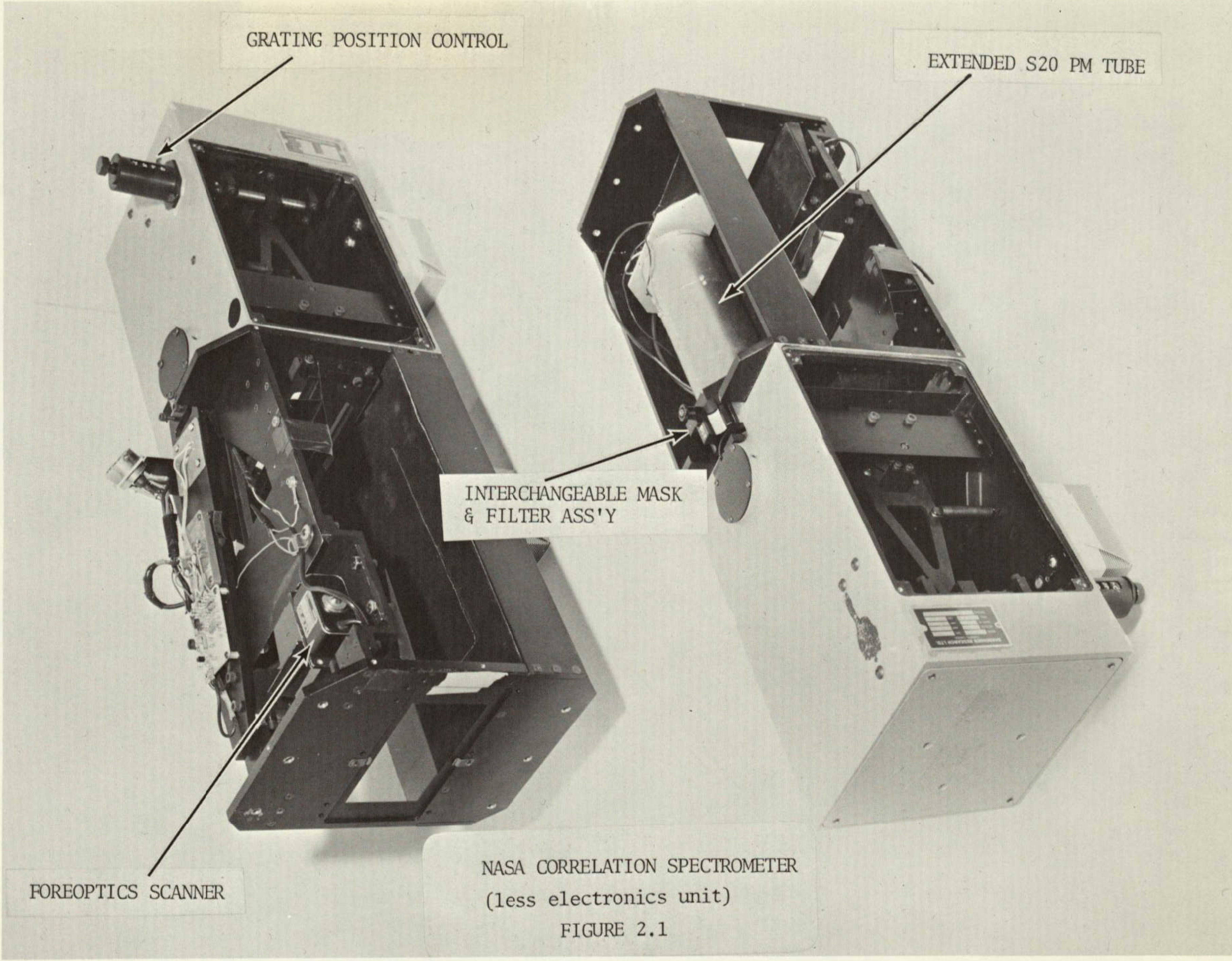
Figure 2.6 shows the NO_2 spectra and bandpass characteristic. I_2 characteristics are shown in Figure 2.7.

A comparison of all three absorption spectra shows the average peak-to-trough separation of SO_2 bands over the useful range to be about 10Å and roughly equal to the peak-to-trough separation on the steepest side of the I_2 bands. NO_2 on the other hand is quite variable over the selected range with the more intense bands having an average separation of 15Å.

To maximize instrument sensitivity for all three gases without the need for changing refractor plates, a fixed special modulation of 10Å was used and the masks for all three gases designed to work over those portions of their respective spectra which would provide maximum contrast in a 10Å interval.

Figure 2.8 shows typical SO_2 calibration curves for three different light levels. These curves demonstrate good linearity well beyond the SO_2 levels commonly encountered in the atmosphere and the small change in curve position caused by a reduction in light demonstrates the ability of the automatic gain control (AGC) to adequately compensate. The small scatter in the data is due more to experimental error rather than AGC error.

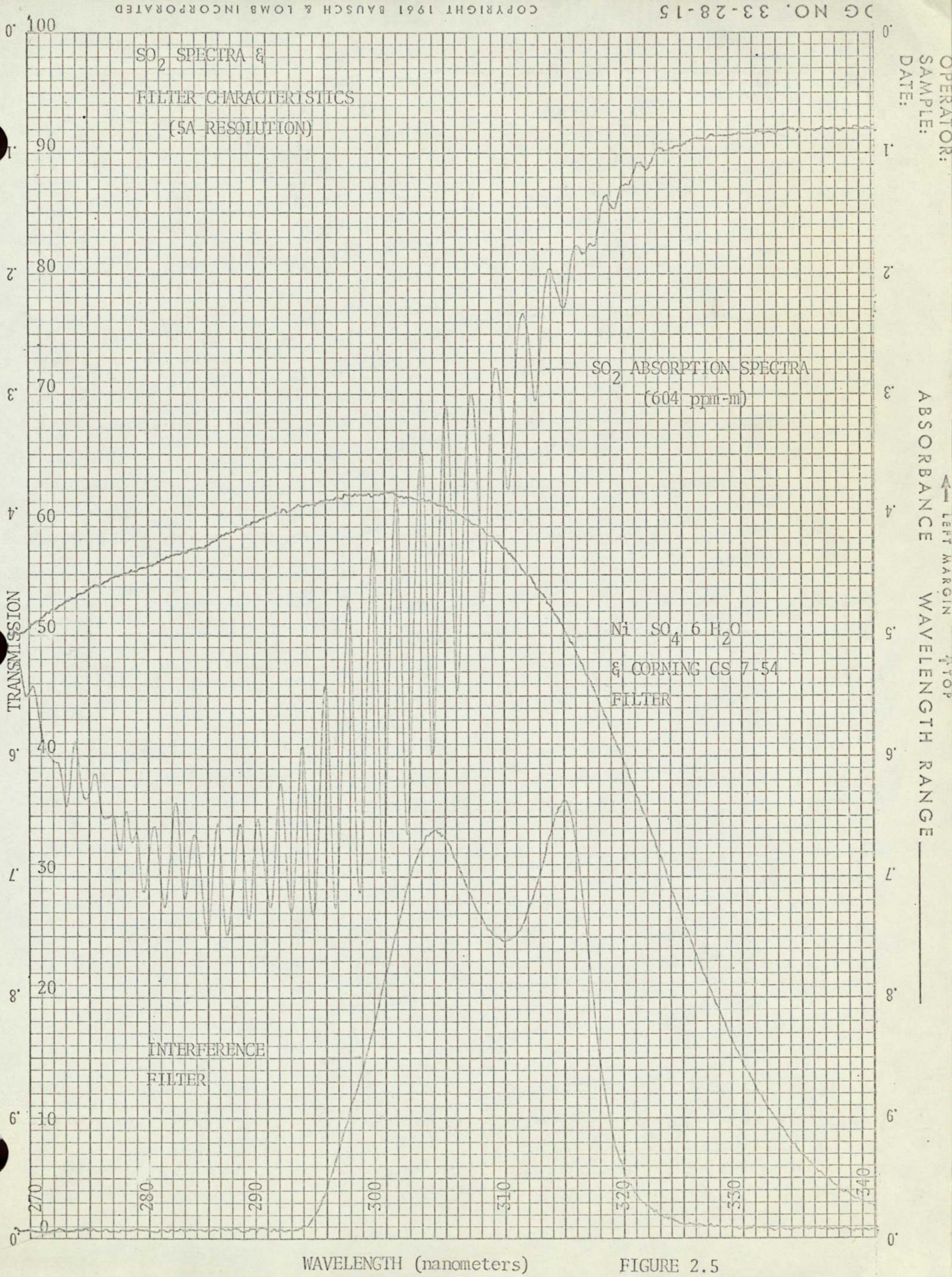
Figure 2.9 shows similar curves for NO_2 and Figure 2.10 for I_2. The I_2 data were obtained by controlled heating of I_2 crystals in a large cell at one atmosphere and calculating ppm from the vapor pressure/temp. curve of Figure 2.11. Only one curve is shown plotted in Figure 2.10. This is because a 90% reduction in light level showed no change in response exceeding experimental error. The heated reference cell used in the airborne tests was always operated at a sufficiently high temperature so as to maintain its charge of I_2 fully vaporized. The value or burden of the cell was 57 ppm-meters.



NASA CORRELATION SPECTROMETER
(less electronics unit)
FIGURE 2.1

Floating Seaweed off the
Coast of Maine

FIGURE 3.6



COPYRIGHT 1961 BAUSCH & LOMB INCORPORATED
OG NO. 33-28-15
OPERATOR:
SAMPLE:
DATE:
SO2 SPECTRA &
FILTER CHARACTERISTICS
(5A RESOLUTION)
SO2 ABSORPTION SPECTRA
(604 ppm-m)
Ni SO4 6 H2O
& CORNING CS 7-54
FILTER
INTERFERENCE
FILTER
TRANSMISSION
ABSORBANCE
ABSORBANCE WAVELENGTH RANGE
LEFT MARGIN
TOP
100
90
80
70
60
50
40
30
20
10
0
270
280
290
300
310
320
330
340
WAVELENGTH (nanometers)

FIGURE 2.5

Matinicus Rock (The most seaward of the Matinicus Group) at low tide August 19, 1968

FIGURE 3.5

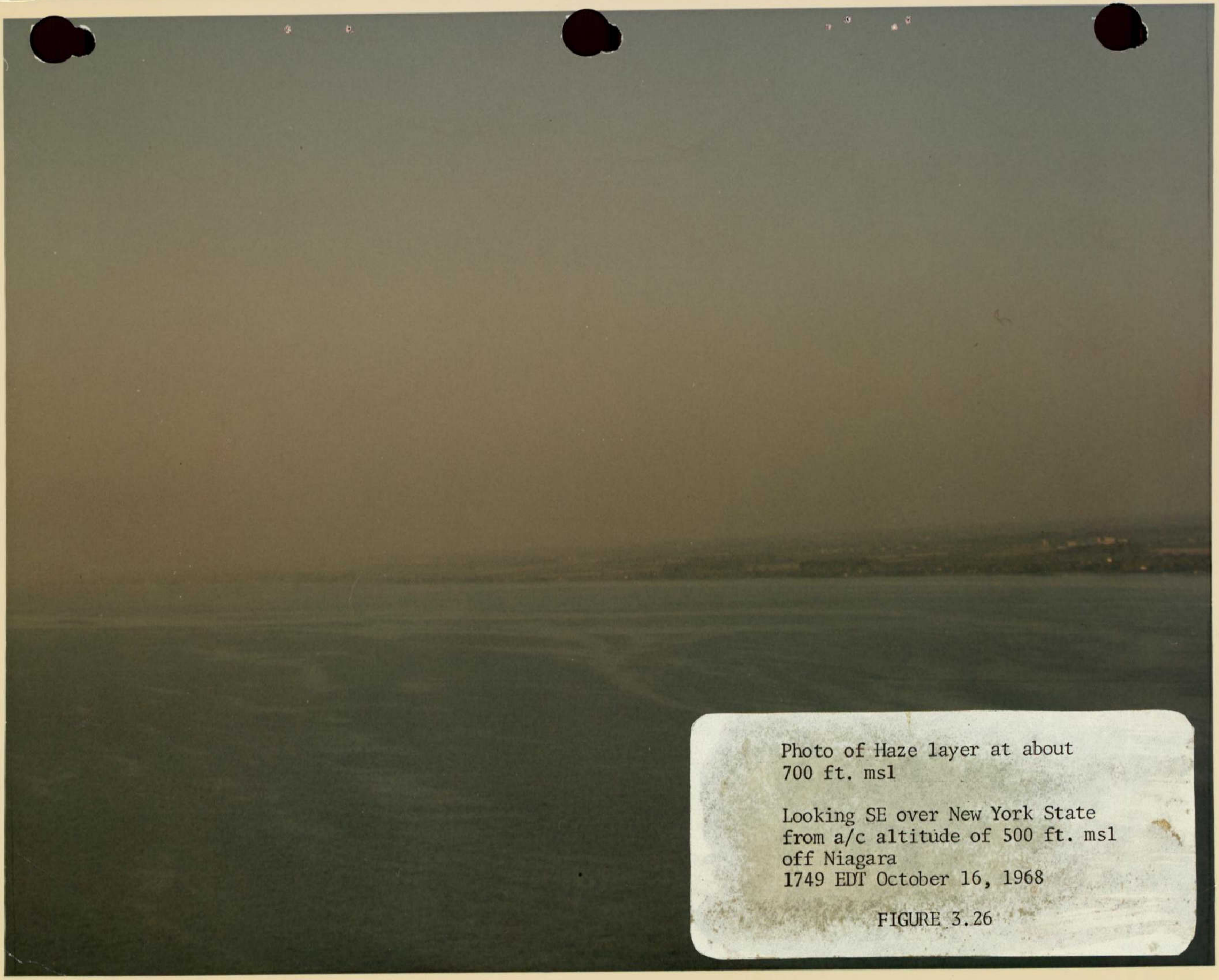


Photo of Haze layer at about
700 ft. msl

Looking SE over New York State
from a/c altitude of 500 ft. msl
off Niagara
1749 EDT October 16, 1968

FIGURE 3.26

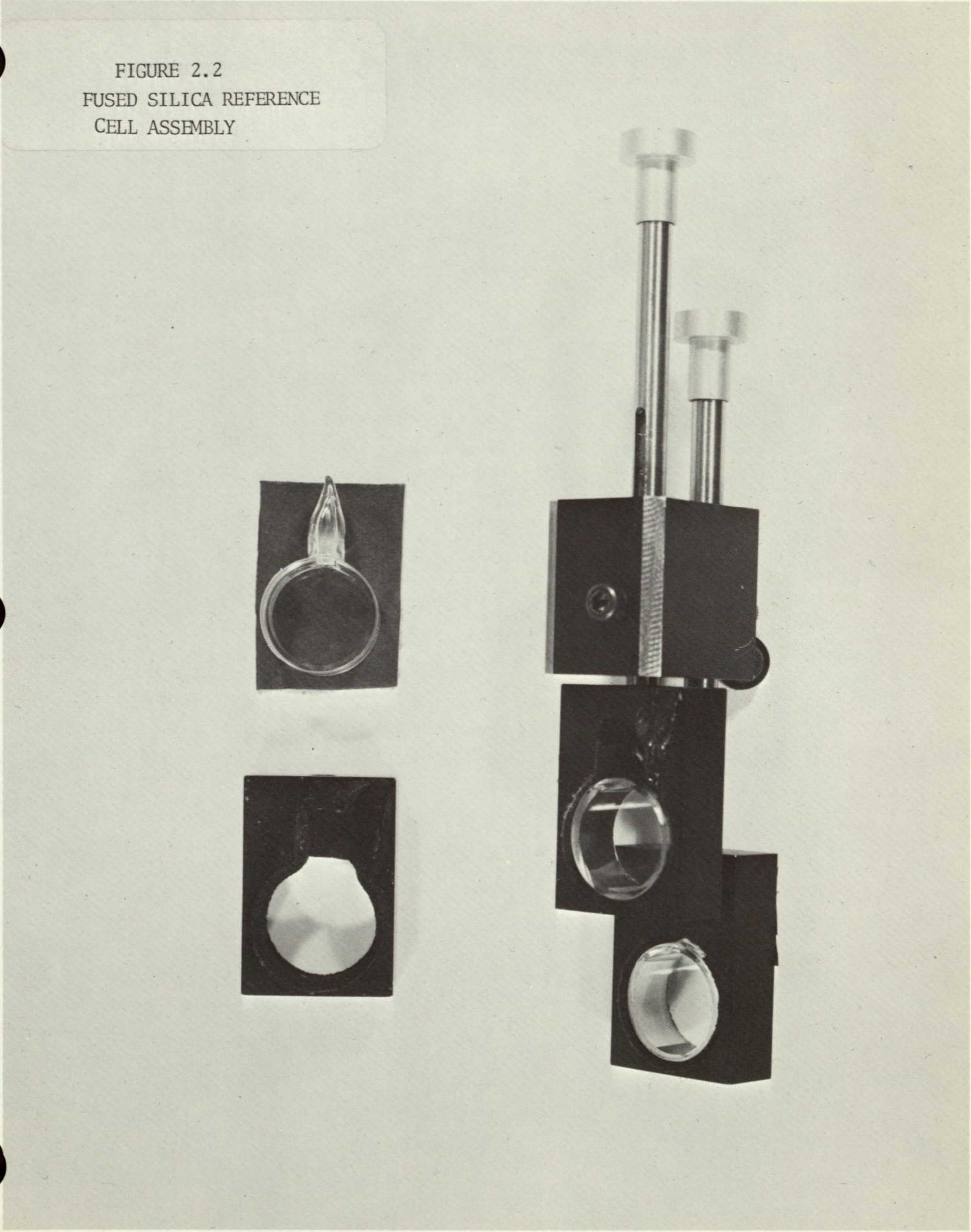
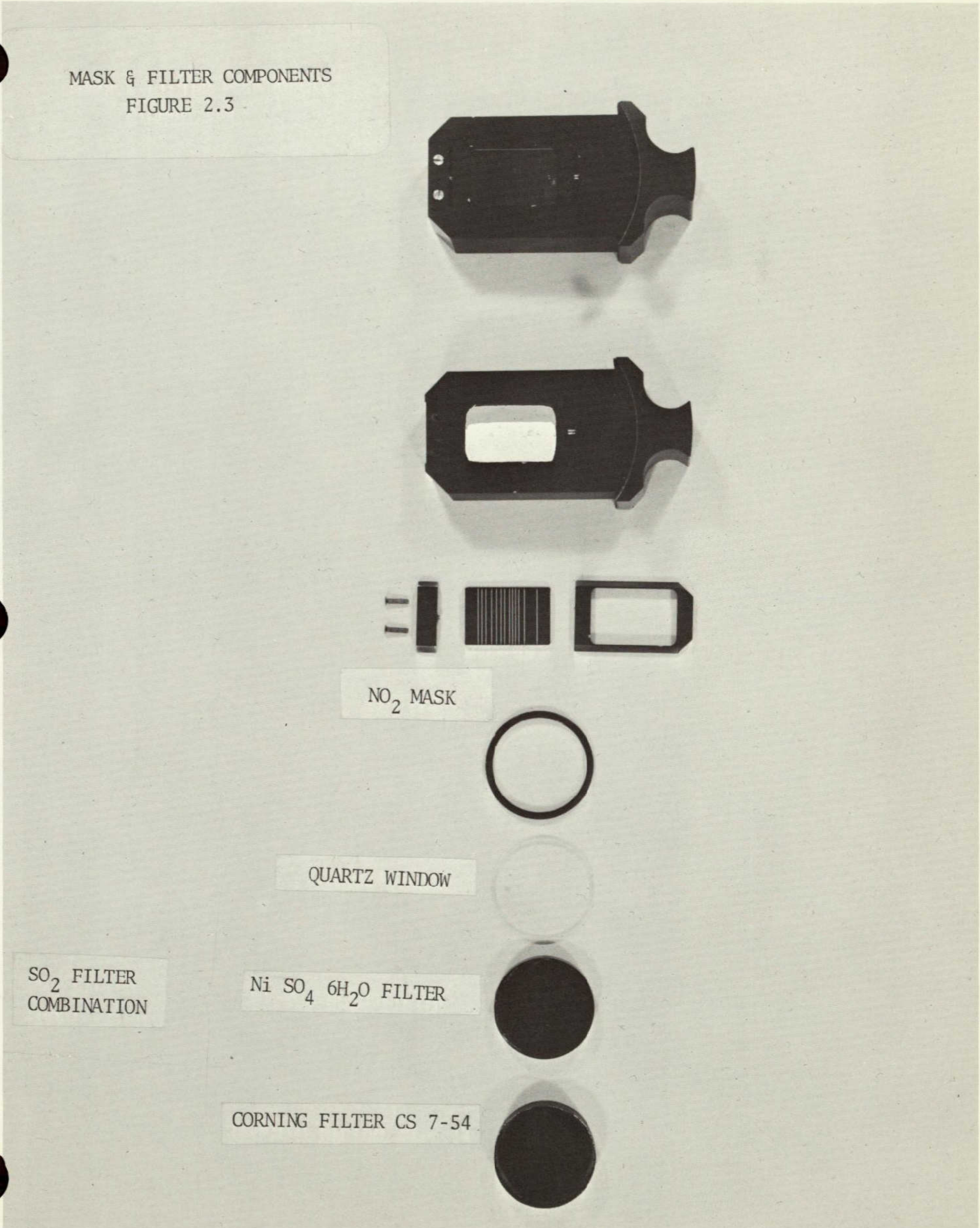


FIGURE 2.2
FUSED SILICA REFERENCE
CELL ASSEMBLY



MASK & FILTER COMPONENTS
FIGURE 2.3

K+E 10 X 10 TO THE CENTIMETER 18 X 25 CM. 46 1513 MADE IN U.S.A.
KEUFFEL & ESSER CO.

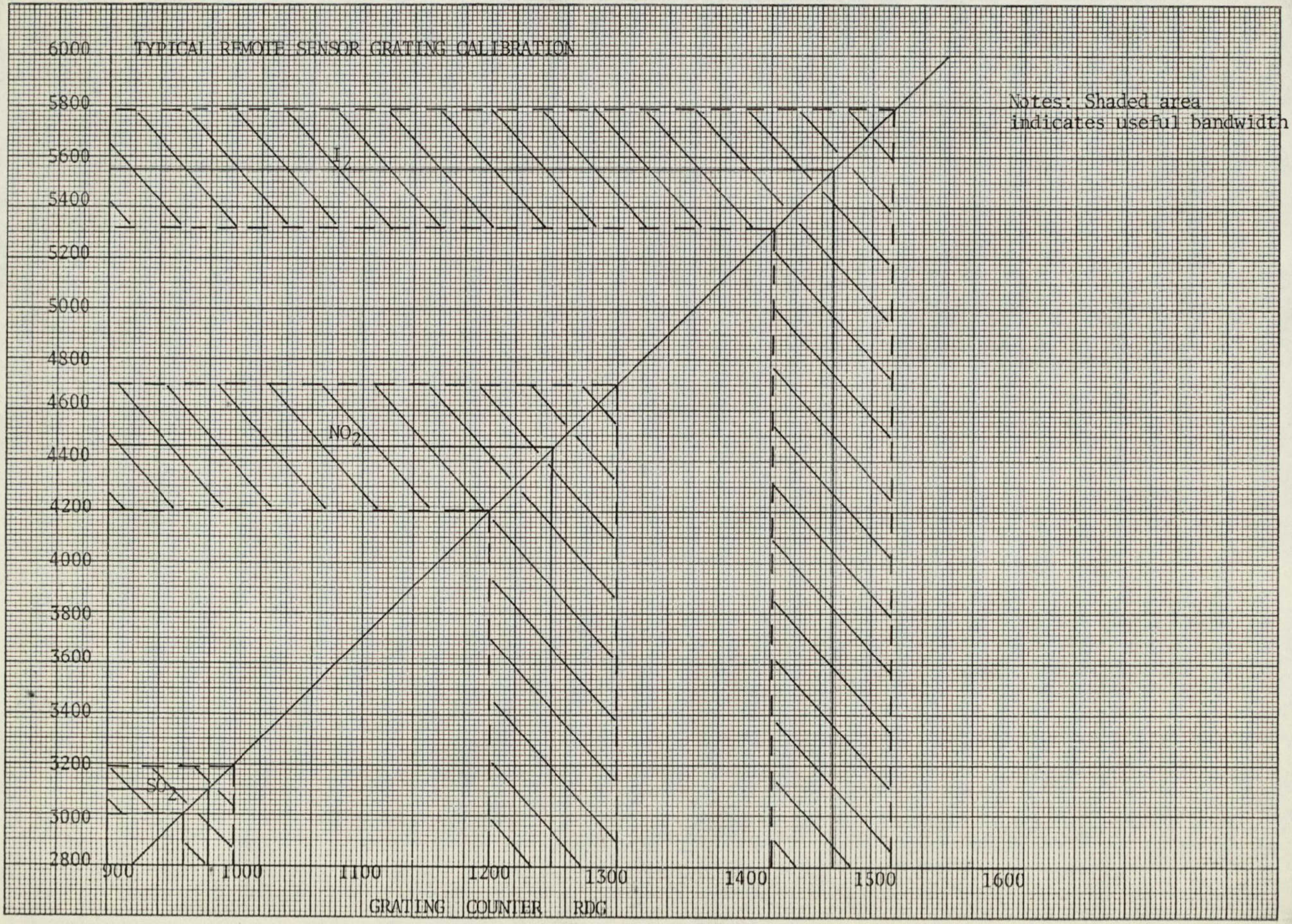
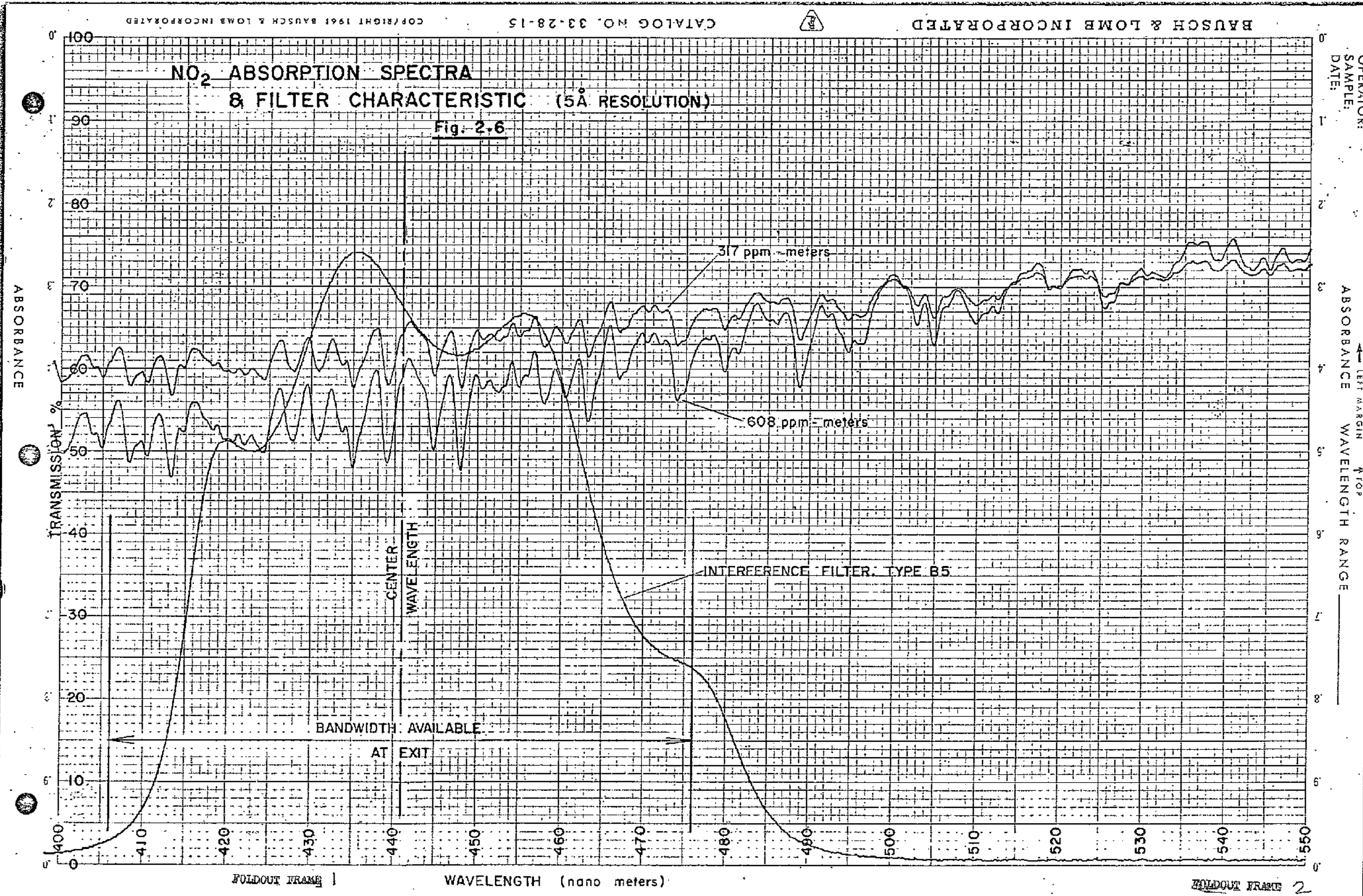
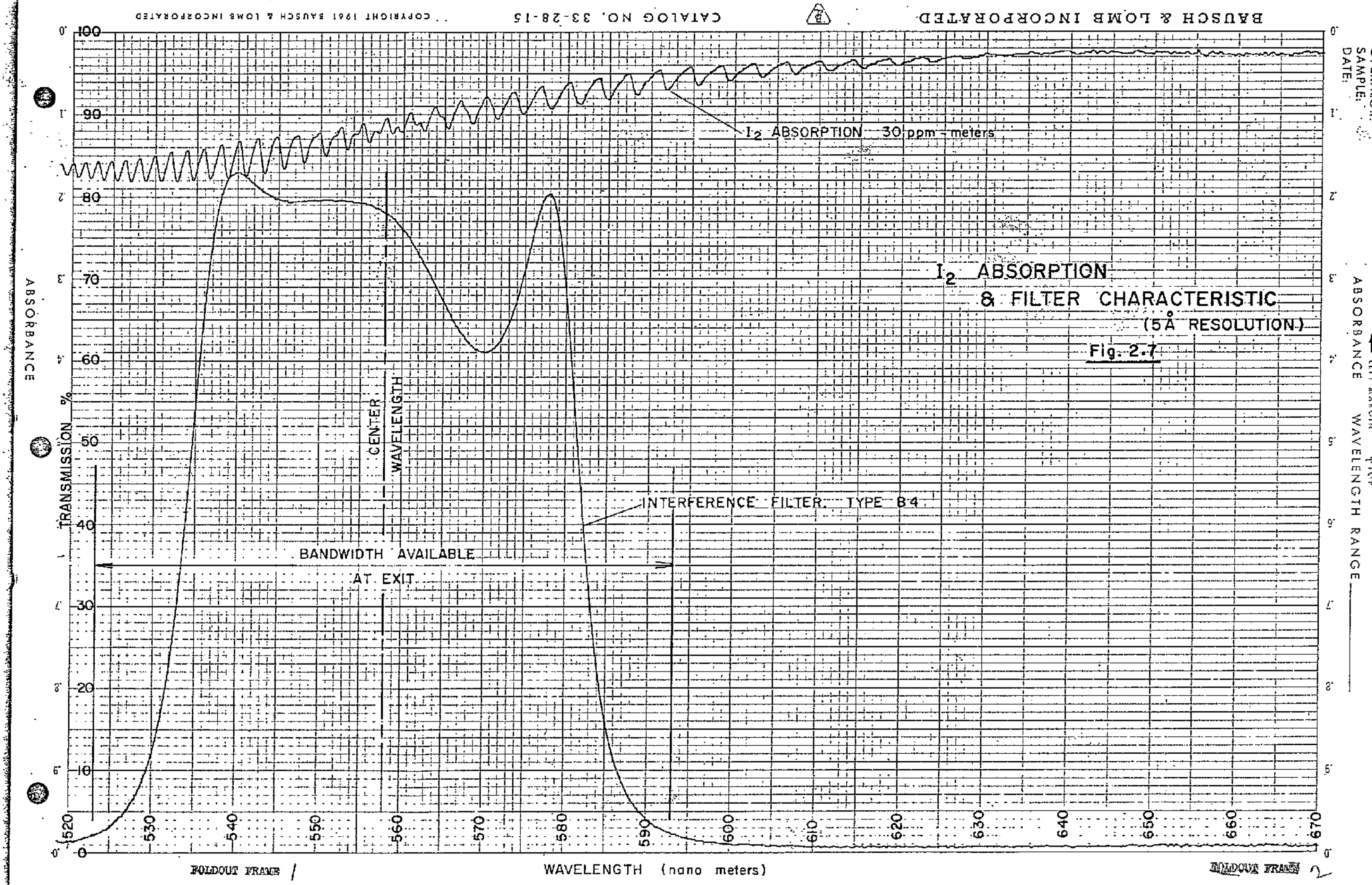


FIGURE 2.4



BAUSCH & LOMB INCORPORATED
CATALOG NO. 33-28-15
COPYRIGHT 1961 BAUSCH & LOMB INCORPORATED
NO2 ABSORPTION SPECTRA
& FILTER CHARACTERISTIC (5Å RESOLUTION)
Fig. 2.6
317 ppm - meters
608 ppm - meters
INTERFERENCE FILTER, TYPE B5
CENTER WAVELENGTH
BANDWIDTH AVAILABLE
AT EXIT
TRANSMISSION %
ABSORBANCE
WAVELENGTH RANGE
OPERATOR:
SAMPLE:
DATE:
100
90
80
70
60
50
40
30
20
10
0
400
410
420
430
440
450
460
470
480
490
500
510
520
530
540
550
WAVELENGTH (nano meters)
FOLDOUT FRAME 1
FOLDOUT FRAME 2



I_2 ABSORPTION & FILTER CHARACTERISTIC (5 Å RESOLUTION)

Fig. 2.7

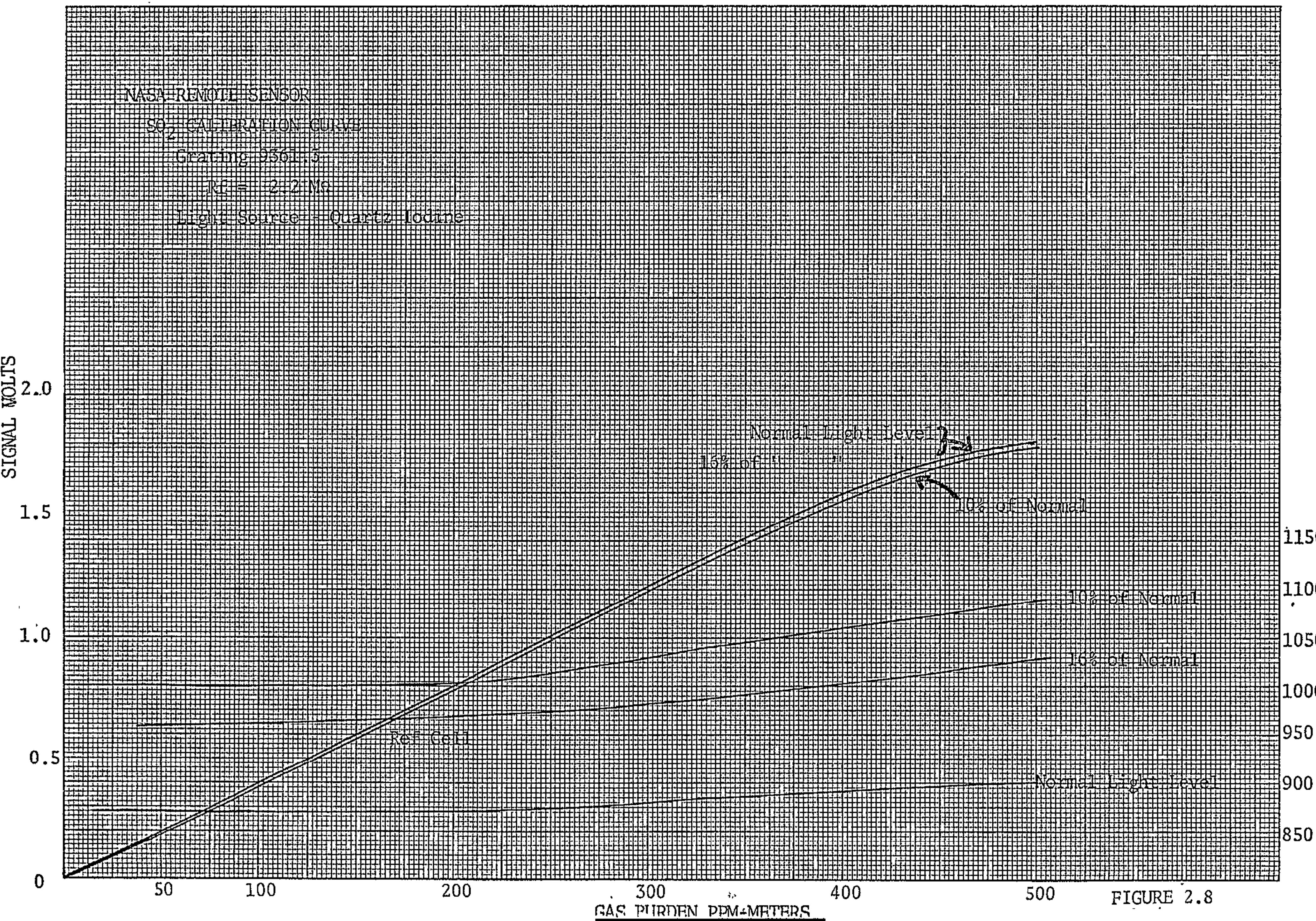

NASA REMOTE SENSOR
SO_2 CALIBRATION CURVE
Grating 9361.3
RF = 2.2 MΩ
Light Source - Quartz Iodine
SIGNAL VOLTS
2.0
1.5
1.0
0.5
0
Normal Light Level
15% of " " "
10% of Normal
10% of Normal
15% of Normal
Ref Cell
Normal Light Level
1150
1100
1050
1000
950
900
850
50
100
200
300
400
500
GAS BURDEN PPM-METERS

FIGURE 2.8

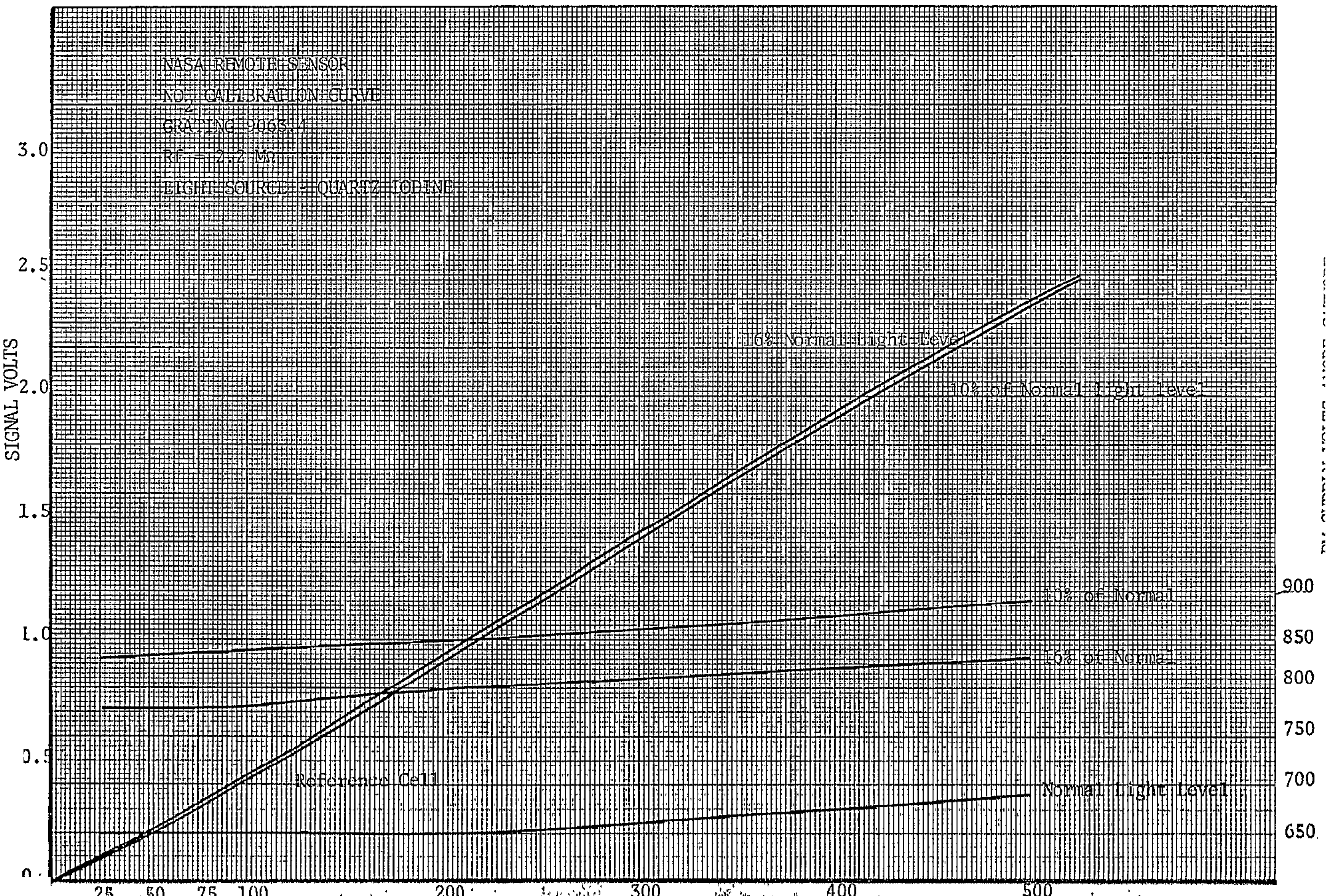

NASA REMOTE SENSOR
NO_2 CALIBRATION CURVE
GRATING 9063.4
Rf = 2.2 MΩ
LIGHT SOURCE - QUARTZ IODINE
SIGNAL VOLTS
3.0
2.5
2.0
1.5
1.0
0.5
0
16% Normal Light Level
10% of Normal Light Level
10% of Normal
16% of Normal
Reference Cell
Normal Light Level
900
850
800
750
700
650
25
50
75
100
200
300
400
500
GAS BURDEN PPM-METERS

FIGURE 2.9

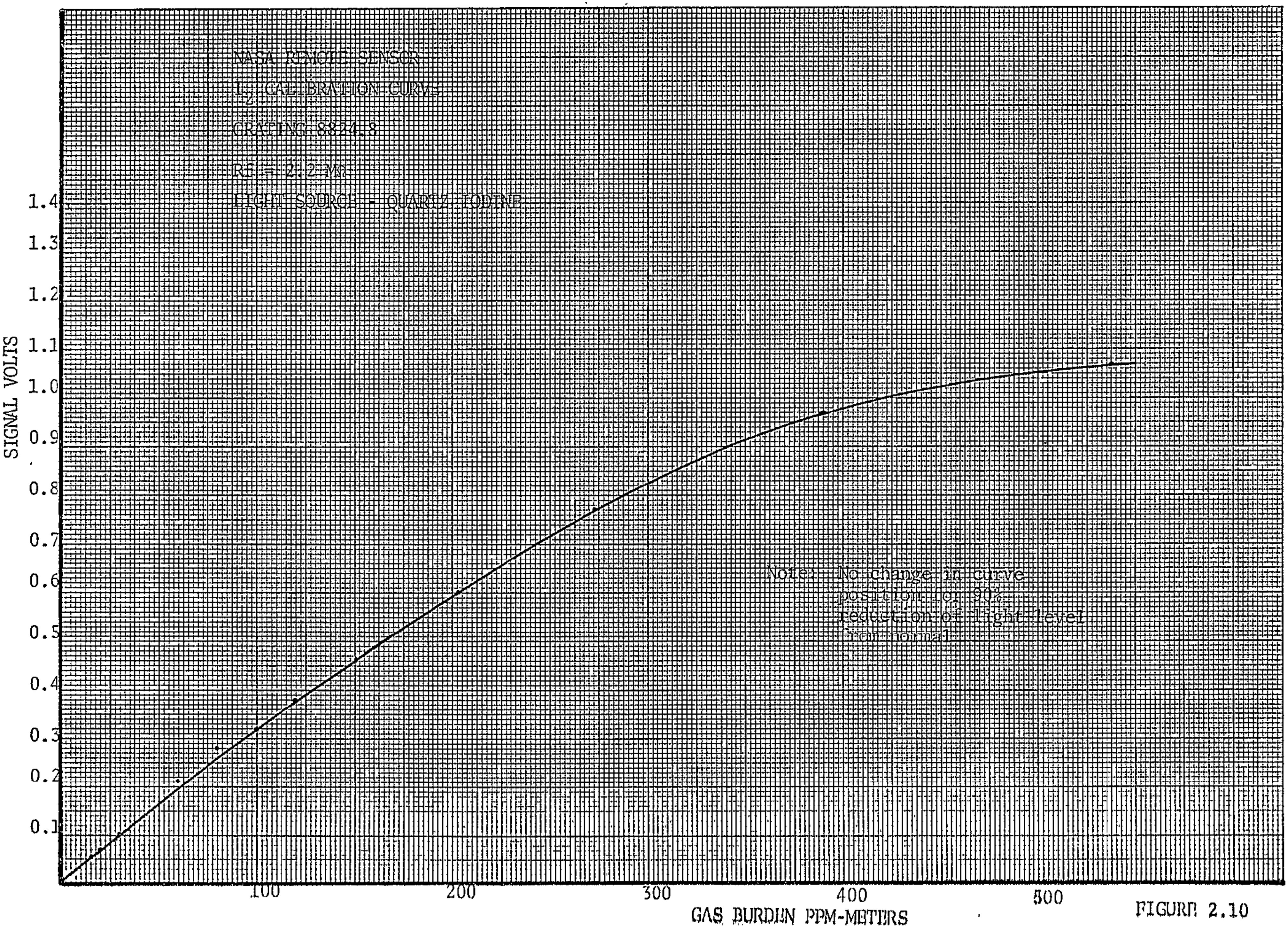
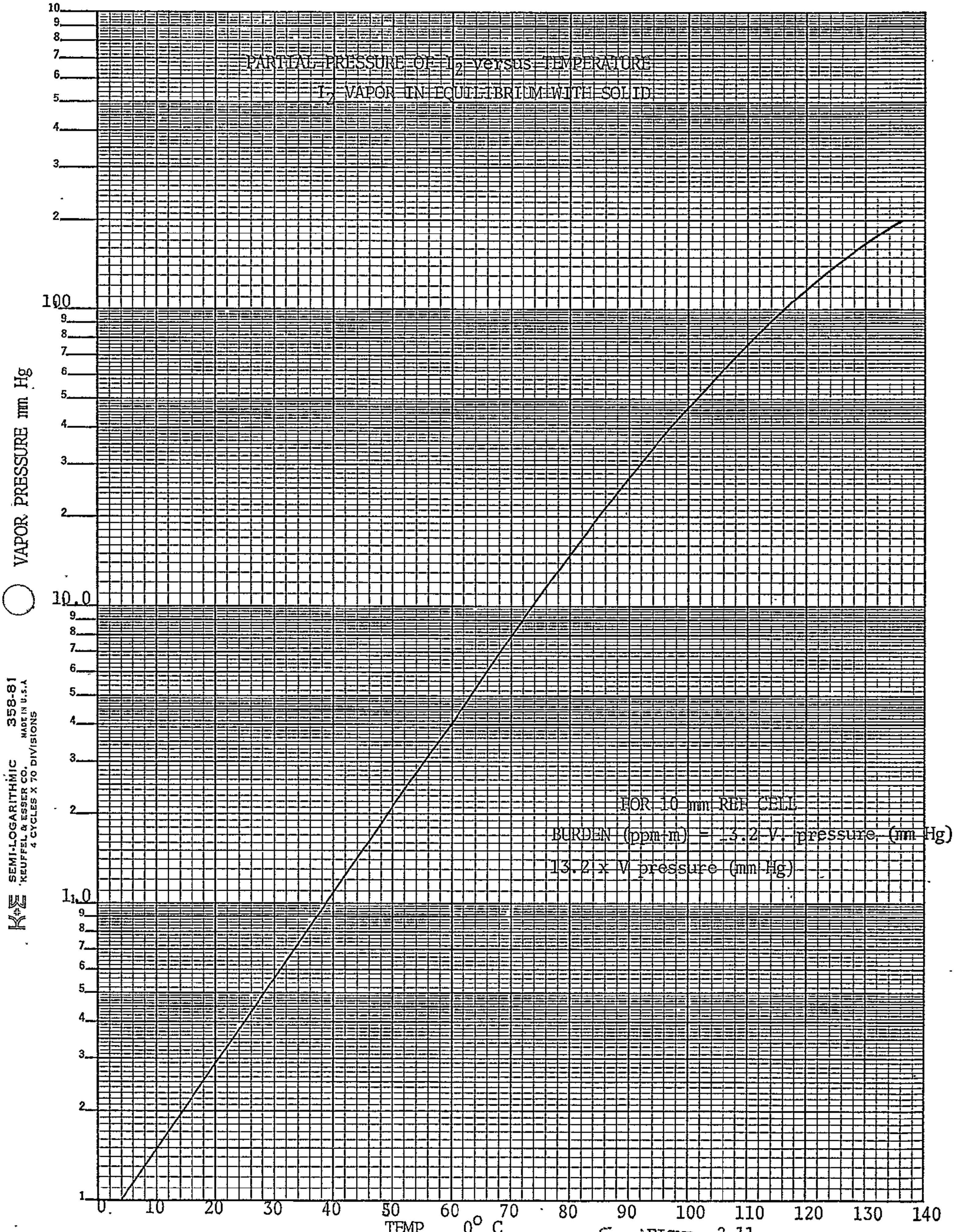

NASA REMOTE SENSOR
I_2 CALIBRATION CURVE
GRATING 8824.8
RF = 2.2 MΩ
LIGHT SOURCE - QUARTZ IODINE
Note: No change in curve position for 90% reduction of light level from normal
SIGNAL VOLTS
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
100
200
300
400
500
GAS BURDEN PPM-METERS

FIGURE 2.10



PARTIAL PRESSURE OF I_2 versus TEMPERATURE
I_2 VAPOR IN EQUILIBRIUM WITH SOLID
VAPOR PRESSURE mm Hg
FOR 10 mm REF CELL
BURDEN (ppm-m) = 13.2 V. pressure (mm Hg)
13.2 x V pressure (mm Hg)
TEMP 0° C
SEMI-LOGARITHMIC 358-81
KEUFFEL & ESSER CO. MADE IN U.S.A.
4 CYCLES X 70 DIVISIONS

FIGURE 2.11

Section 3

FLIGHT RESULTS

3.1 Los Angeles NO_2/SO_2 Survey

The results of this survey have been reported on previously[1]. Very briefly, the most significant features of the Los Angeles program were the close agreement between airborne and ground level (APCD) measurements with respect to synoptic distributions. In particular, for NO_2 direct comparisons of the two sets of measurements showed the airborne (average) result to be about 1/3 the APCD value which appears very reasonable considering the great differences in the two methods.

3.2 I_2 Flight Tests, Coast of Maine (Aug. 10-13th/68)

A total of six flights were accomplished during which I_2 detection was attempted. These include the ferry flights into and out of the New England area and an initial exploratory flight along the Massachussetts - New Hampshire coast. The ferry flights were non-productive of useful data because of weather conditions and the flight along the New Hampshire coast failed to show detectable levels of I_2. The three flights described herein showed significant and consistent I_2 responses indicating a build-up of atmospheric iodine with maximum levels indicated in the vicinity of the Matinicus Islands off the Maine coast. These flights are summarized in Tables 3.1 to 3.3 and illustrated in Figures 3.1 to 3.3.

Before discussing the results it is worthwhile to briefly consider some aspects of the iodine detection problem. Firstly, the coast of Maine was selected as a test site because of the abundance of kelp and rockweed which grows in profusion along the coast between the high water mark on shore and over the ocean floor out to depths of several hundred feet. The concentrations of free iodine vapors produced by marine plant is not known, but with a spectrometer noise level of 5 ppm-meters and an effective path length of say 5,000 meters, average concentrations as low

I_2 TRAVERSES - SUMMARY

FLIGHT 3

TABLE 3.1

TIME EDT	RUN/LINE	DIR.	ALT. (ft)	MODE	RESULTS
12.13	1/1	S-N	3,500	SIDELOOK	No significant change in background
12.27					level.
12.33	2/1	N-S	2,500	SIDELOOK	Increase of 13 ppm meters from Long
12.54					Isle to Matinicus.

TAKE-OFF, HANSCOMB FIELD 11.12 A.M. EDT

TEMP - 18°C

ALTIMETER SETTING 29.89 'Hg

WIND _ LIGHT AND VARIABLE AT 0° (by observation)

LAND - 1.44 P.M. E.D.T.

I_2 TRAVERSES - SUMMARY FLIGHT 4.

TABLE 3.2

TIME	RUN/LINE	DIR.	ALT(ft)	MODE	RESULTS
E.D.T. 8.37 - 9.07	1/1	S-N	2,500	LOOKDOWN	30 ppm meters increase from Monhegan-Long Isle
9.10 - 9.27	2/1	N-S	1,000	SIDELOOK	Rise of 10 ppm meters, Long Isle to Matinicus. Decrease of 20 ppm meters, Matinicus to Monhegan
9.19-9.43	3/2	S-N	1,000	SIDELOOK	No signifant change
9.49-10.02	4/3	N-S	500'	SIDELOOK	Rise of 13 ppm meters from Long Isle to Matinicus Rock.
10.07-10.21	5/4	S-N	500'	SIDELOOK	Rise of 16 ppm meters from Monhegan to 2 miles NE of Matinicus (floating seaweed)
10.25-10.40	6/2	N-S	500'	SIDELOOK	No significant change though background 5 ppm meters higher in vicinity of floating weed.
10.42-10.46	7/2	S-N	500'	SIDELOOK	No significant change.
10.50-11.02	8/5	N-S	500'	SIDELOOK	Decrease of 26 ppm meters from just NW of Matinicus to Monhegan.

TAKE-OFF	PORTLAND 8.27 A.M. E.D.T
PRESS.	29.96 "Hg.
TEMP.	65° F.
WIND	280° Approx.
LAND	11.20 A.M. E.D.T.

2 TRAVERSES - SUMMARY FLIGHT 5

TABLE 3.3

TIME	RUN/LINE	DIR.	ALT.	MODE	RESULTS
EDT					
3.26-3.33	1/1	INBOUND	2,500'	SIDELOOK	No significant change.
	2/1	OUTBOUND	2,500'	SIDELOOK	17 ppm meters increase from 4 miles West of Portland to Lightship.
3.37-3.46	3/1	INBOUND	2,500'	SIDELOOK	14 ppm meters decrease from Lightship to South Windham.
WIND 280					
3.52-4.44	4/1	OUTBOUND	3,500'	SIDELOOK	14 ppm meters in increase from West End of traverse to Lightship.
4.15-4.27	5/2	INBOUND	2,500'	SIDELOOK	12 ppm meters decrease from 8 miles SW of Monhegan to Lisbon Falls
4.45-5.01	6/3	OUTBOUND	2,500'	SIDELOOK	23 ppm meters increase from Augusta to Matinicus.
5.02-5.20	7/4	INBOUND	2,500	SIDELOOK	9.5 ppm meters decrease from Matinicus to Small Pt. Beach.

TAKE-OFF - 2.59 P.M. - E.D.T. PORTLAND

TEMP.

PRESSURE

WIND .16 mph @ 280°

LANDING - 5.40 P.M. E.D.T.

as several parts per billion could be detected. With the present spectrometer configuration however, the measurement of absolute levels is not possible because of errors induced by changes in the spectral distribution of incident radiation. It is therefore not possible to zero the instrument against an I_2 free radiation source such as a lamp or the overhead sky. For purposes of this series of flight tests therefore the procedure was to fly at low altitude with the spectrometer looking sideways and the line of sight tilted down about 10° below the horizontal. In this way the effect of spectral changes is minimized and the effective path length is maximized.

By appropriate choice of flight lines it is then possible to detect changes in total I_2 burden, as scanned by the airborne system with a resolution of 5-10 ppm-meters. Sensitivity of the spectrometer was measured periodically by inserting a calibrated reference cell temporarily into the optical path of the instrument.

The method used to search for I_2 in flight was then to run a continuous profile of the spectrometer output signal over the full length of a traverse with the spectrometer in the "side looking" mode (except for Flight 4, Run 1 when the vertical mode was used) and then to later analyze the trace for significant anomalies or trends. The location and direction of each traverse was so chosen as to reveal differences between expected low and relatively high levels of I_2. A brief discussion of each flight follows:

Flight 3, Table 3.1, Figure 3.1

The northbound traverse showed a very constant background level indicating no substantial difference in total I_2 within view of the "starboard looking" spectrometer over the length of the run. On the southbound leg however, the trace indicated a steady build-up of I_2, reaching a peak in the vicinity of Matinicus Island and then falling off to a level of 16 ppm-meters lower at Monhegan Island. Note that only changes in signal level which occur over the duration of any one traverse are significant. A comparison of absolute levels between any two traverses is not valid

because of possible differences in spectral gradients as previously explained.

Flight 4, Table 3.2, Figure 3.2

Note that the first run of this flight was made with the spectrometer in the vertical or "look-down" mode. In this case, as on other occasions when the vertical mode was attempted, the background fluctuation was relatively high. A portion of the strip chart recording from this run is shown in Figure 3.4 (c).

The purpose of flying traverses on either side of Matinicus Isle was to determine if it was possible to break out the Matinicus group as a distinctive I_2 anomaly. Figure 3.2, shows the flight lines and the traverses, or runs during which significant changes in I_2 level were observed. The first run using a vertical look shows the I_2 level in the vicinity of Long Isle to be 30 ppm-meters higher than I_2 levels around Monhegan. On the second run, using the side-look mode, the background level tended to rise slightly from Long Isle to Matinicus (10 ppm-meters) but showed a definite drop (20 ppm-meters) from Matinicus to Monhegan. The same trend in I_2 levels was observed on runs 4,5, and 8. Note that no significant changes were noted on runs 3,6 and 7 indicating either that no significant quantity was observed, or what is more likely, that the I_2 vapors were so dispersed as to show no significant change in total burden over the duration of the run. Note that runs 3,6 and 7 are all upwind of the Matinicus group.

Flight 5, Table 3.3, Figure 3.3

The traverses shown in Figure 3.3 were designed to reveal a coastal I_2 anomaly. Note that there is a gradual but consistent build up of I_2 off the coast which is independent of aircraft heading. The absence of a more abrupt change or a more distinctive anomaly can be explained by the extremely irregular shoreline and the gradual transition to a marine atmosphere. Unfortunately the traverses could not be extended out to sea without violating National Defence prohibited

air space. The first run was spent largely in making instrument adjustments and the fact that no significant trends in the I_2 levels was noted is not too significant.

A typical example of the strip chart recording for Flight 5 is shown in figure 3.4 (a). The chart reads in increasing time from right to left and shows an increase of 23 ppm-meters in background I_2 level from Augusta to Matinicus. For an assumed 5,000 meter path length this would represent a background I_2 level some 5 parts per billion higher in the vicinity of Matinicus than in the vicinity of Augusta.

Determination of Free Iodine & Total Iodine in Seaweed

Wet chemistry measurements of very low I_2 concentrations in the atmosphere are difficult to make and a comprehensive series of measurements of the scope required to confirm the remote sensor results would be a major undertaking. On the other hand measurements of the I_2 content of seaweed, although not as convincing as measurements in the free vapor phase, are very much simpler to make. For the sake of ground truth then, a sample of rockweed was obtained from the rocky coastline of Maine during the I_2 flight program and analyzed in the BRL laboratories. The following describes the procedure followed and the results obtained:

Free Iodine: - A 3 gm. sample of seaweed was placed in a U-tube, which took the place of the U-tube containing Iodine Pentoxide, in a set-up more usually used for the determination of carbon monoxide in samples of gases.

This U-tube has provision for being heated to 160°C and was followed by a bubbler containing 3% KI solution. The seaweed was heated to 160°C while being swept with dry, CO_2 free air. Any free iodine present would have been vapourized and absorbed in the KI solution, where it could have been determined by titration with $\frac{N}{1000}$ sodium arsenite, using fresh starch indicator. Although the KI solution assumed a brown colouration on running the test, no iodine was present, as no blue colour was produced on adding the starch indicator.

From considerations of sensitivity of the method and the amount of seaweed sample taken the minimum detectable level of I_2 was calculated and found to be less than 5 ppm- W/W. This means that if free I_2 was present in the sample it would have to have been less than 5 ppm W/W.

Total Iodine

Over 50 grm. of seaweed was initially taken. This was ashed completely in a Nickel crucible in the presence of sodium carbonate, which combined with the potassium carbonate present in the seaweed ash to give a clear, quiescent melt. This melt was dissolved in dilute HCL, and the resulting solution made to 1% $^V/_V$ conc. HCL/water.

The iodide was then precipitated as palladous iodide with palladous chloride solution, following the method on P. 493 of Reference (10).

The precipitate was allowed to stand for 24 hours, then filtered through a fine, sintered glass, crucible, and then washed 4 times with warm water, after which it was oven dried @ 100°C for 1 hour.

From the weight of Pd I_2 obtained, and the original weight of seaweed taken, a value of:

0.140% $^W/_W$ Total Iodine was obtained (as received).

From the loss of weight on drying a further sample of seaweed, a figure of:

0.156% $^W/_W$ Total Iodine (Dry Basis) was obtained.

DISCUSSION OF I_2 RESULTS

The improvement in signal-to-noise ratio of the side-look relative to the vertical mode is readily seen in Figure 3.4. A three second integration time was used for Figure 3.4 (a) and (b) and one second integration time for Figure 3.4 (c). Comparing figures 3.4 (a) and (b), the internal system noise is the same but the background fluctuation, or total noise appears to be 2-3 times higher for the vertical mode over the side-look mode.

The very substantial offset produced by differences in spectral gradient between sky radiation and radiation reflected from the oceans surface is evident in Figure 3.4 (c). Proceeding from right to left, an offset of 53 ppm-meters was recorded when switching from sky to water. The reason for this offset as mentioned earlier, is inherent in the instrument mechanization and is explained fully in Appendix I. The new instrument design proposed in Section 4 should overcome this deficiency or at least greatly reduce it.

Figures 3.4 and 3.6 are 35 mm photographs taken from Aero-Commander. Figure 3.5 shows Matinicus Rock, the most seaward member of the Matinicus group. The visible rockweed growth along the shore is typical of most of the rugged Maine coastline.

Figure 3.6 shows seaweed floating freely on the oceans surface in the vicinity of the Matinicus Islands. Many such sightings were made during the course of the program.

The laboratory analysis of the seaweed sample confirmed the presence of a significant concentration of total I_2 in the plant but free I_2 was undetected. The absence of free I_2 is not surprising since the weed sample was stored in unsealed containers in a semi-dehydrated state for several months before analysis could be made. This is more than enough time to permit the escape of any free I_2 originally stored in the plant.

The following points may be used to summarize the findings of the I_2 flights.

(1) Data runs consistently showed higher levels of atmospheric I_2 along the coast than further inland.

(2) On the days of flights, the I_2 levels in the vicinity of Matinicus Isle appeared to be significantly higher, in a relative sense, than I_2 levels elsewhere along the coast.

3.3 CHATTANOOGA NO_2/SO_2 SURVEY

Synoptic distributions and plume chases for NO_2 and a plume chase for SO_2 were conducted in the Chattanooga area on behalf of the National Air Pollution Control Administration (N.A.P.C.A.) in the period August 3rd to August 7th. The results of the survey are reported in reference (2). It is useful however to discuss here certain aspects of the Chattanooga data, namely instrument and background noise levels. Moreover it is preferable to use these data rather than the Los Angeles data for this purpose because of improvments made to the equipment following the Los Angeles program (see Section 2). Two of the most significant improvements from noise stand-point were (a) more effective vibration isolation of the mirror system and (b) improved light baffling within the aircraft mounting fixture. These modifications resulted in a marked improvement in system stability and measurement repeatability. The system performance as demonstrated in all subsequent flights represents the true capabilities of the correlation spectrometer at its present level of development.

Figures 3.7 and 3.8 illustrate typical noise characteristics of the NO_2 and SO_2 channels respectively. Note that the minimum detectable signal in both channels is limited by two very different types of noise namely, (1) internal instrument noise, which is a combination of photon noise and synchronous detector noise and (2) external noise, which is a complex function of many variables in the total measurements. The most significant component of external noise is believed to be both short and relatively long term variations in spectral distribution or gradient. This is discussed further in Section 3.7. From Figures 3.7 and 3.8 it is apparent that internal noise is about 8 ppm-meters for NO_2 and 10-15 ppm-meters for SO_2. The external noise is the slow, irregular signal fluctuations. For NO_2 over varied tree and brush covered terrain with water patches and cultured, or built-up areas, the external noise is approximately 15 ppm-meters and for SO_2 about 20 ppm-meters.. Both of these values are for an aircraft altitude of 8,000 ft. External noise tends to decrease with increasing aircraft altitude.

3.4 PLUME CHASE EXPERIMENTS

A "plume chase" is a series of airborne measurements of effluent from a concentrated source of emissions, such as one or more chimneys or stacks, at various distances from the stack exit(s). The primary purpose of the plume chase experiment is to provide data which will permit the accuracy of the remote sensing technique to be determined. It is the simplest and perhaps the most accurate way of comparing the remote sensing method quantitatively with other established and proven methods. The plume parameter of first interest here is the mass flow rate.

A successful plume chase experiment requires a rather stringent set of plume and environmental conditions, namely;

(1) A straight horizontal plume with a low dispersion or spread angle.
(2) Adequate clearance between the plume and ground for aircraft flight.
(3) Absence of competing sources of emission.
(4) Flat and uniform topography under the plume
(5) Absence of low cloud cover.
(6) Adequate solar illumination.
(7) No low level (legal) flight restrictions.

The geography of the Toronto area water-front offers many of the above noted prerequisites. Lake Ontario provides a strong positive influence for the stable air conditions required for an undisturbed plume, a singularly potent source of emissions is available at the Ontario Hydro Lakeview Generating Station with no competing sources downwind from it (assuming a westerly wind) and there are no low level flight constraints over the lake surface. Unfortunately during the last two months of this experimental program (October and November), adverse weather conditions severly restricted the opportunities for plume chase experiments. Low lying cloud is particularly objectionable for a precise test of this kind since it may not only restrict the view of the plume, but it also promotes instability and convective mixing in the layer of air between it and the ground.

The first flight results discussed below (August 27/68) was actually conducted under NAPCA contract NO. PH22-68-44 but are presented here because of their pertinence.

August 27/68 NO_2 Plume Chase

Figure 3.9 shows the plume outline and the aircraft flight lines for a series of NO_2 measurements of the effluent from Lakeview Generating Station. A photo of the Generating Station from a previous flight is shown in Figure 3.10. Wet chemistry measurements were made at the source simultaneous with the airborne measurements. Figure 3.11 shows the actual strip chart profiles of two traverses over the plume and Table 3.4 lists the data obtained. Figure 3.12 illustrates, in a simplified form, all plume profiles obtained. All traverses of the plume were made above the plume and at right angles to the plume center line at an aircraft altitude of 1,525 meters (5,000 ft.). The build up of NO_2 with distance or time is evident. A peak value of 76,800 ppm-m^2 was obtained at 16 Kilometers from the source. Mass flow may be found as follows:

$$\text{Mass flow} = \text{Plume Cross Section (ppm-m}^2) \times \frac{1}{\text{m-factor}} \times \text{wind velocity} \times \text{gas density (gms/m}^3) \times 10^{-6}$$

Plume Cross Section = 76,800 ppm-m^2

Wind velocity = 6.71 to 9.40 meters/sec

NO_2 gas density = 1.95 gms/liter @ 70° F and 1 atm. (single molecule)

m factor = 2.49 from NO_2 atmospheric model for 45° latitude Aug. 28th solar zenith angle- 41°

$$\text{then mass flow} = 76.8 \times 10^3 \times \frac{1}{2.49} \times (6.71 \text{ to } 9.40) \times 1.95 \times 10^3 \times 10^{-6} = 403 \text{ to } 565 \text{ gms/sec}$$

$$= 1.61 \text{ to } 2.25 \text{ tons/hr}$$

PLUME CHASE DATA - LAKEVIEW GENERATING STATION - AUGUST 27, 1968

TRAVERSE NO.	DISTANCE FROM SOURCE (Km)	PROFILE LENGTH (cm)	HORIZONTAL SCALE $\left(\frac{\text{meters}}{\text{cm}}\right)$	PROFILE AREA (cm^2)	PROFILE HEIGHT (AVERAGE) (cm)	PLUME CROSS SECTION ($ppm\text{-}m^2$)
1	0.8	1.1	287	2.4	2.18	5,350
2	3.2	3.0	287	5.0	1.67	11,150
3	5.6	8.1	287	10.8	1.34	24,100
4	8.0	5.7	287	14.0	2.46	31,200
5	10.5	8.4	287	27.0	3.21	60,200
6	12.9	9.5	287	30.5	3.21	68,000
7	15.3	11.6	287	34.4	2.97	76,800
8	17.7	9.2	287	34.2	3.72	76,200
9	12.9	8.7	296	21.0	2.41	48,300
10	8.0	4.8	290	6.2	1.29	14,000
11	3.2	4.8	290	6.3	1.31	14,200

Vertical Scale (All Traverses) = 7.77 ppm-m/cm.

Plume Cross Section

= Profile Area x Vertical Scale x Horizontal Scale

= 2.4 x 7.77 x 287

= 5,350 $ppm\text{-}m^2$

TABLE 3.4

The assumption is made in the above calculation that the plume is sufficiently wide in the area of the measurement (3,330 meters) that the atmospheric model (which assumes a distributed homogenous gas layer) is valid. If this assumption is not entirely correct then the above answer would tend to be lower than the actual value.

Ground Truth at Lakeview G.S.

Ground truth measurements were made at the base of one of four stacks of the Lakeview Generating Station using the Phenol Disulphonic Acid method. Commencement of airborne and ground measurements was co-ordinated by preflight briefing and visual signals from the aircraft at the start of the first traverse. The method of determining NO_2 concentration and therefore total amount of NO_2 emitted in stack gases is as follows:

The NO_2 concentration is obtained by allowing a known value of stack gas to enter an evacuated glass flask containing an acid-peroxide absorbing solution

After allowing 24 hours for absorption to reach completion, the NO_2 and potential NO_2, (e.g. NO), is present in the absorbing solution as Nitric Acid. This is neutralized with caustic soda solution, and the absorbing solution, now containing the NO_2 and NO as sodium nitrate is compared colourimetrically with known potassium nitrate standards by means of the absorption at 4200 Å of the phenol disulphonic acid/nitrate complex formed with the sodium nitrate, or potassium nitrate standards. The absolute amount of NO_2 and potential NO_2 presents in the stack gases is calculated from the ppm $^{v}/_{v}$ concentration readily obtained from the above coulorimetric method, and the total gaseous emission from the various stacks.

In the case of Lakeview Generating Station this emission is calculated from figures kindly supplied by Ontario Hydro, giving the lbs/hr. of air fed to the generator units. and the tons/hr of coal fed to the units, together with a complete analysis

of an average sample of the fuel they use. From these figures it is possible to calculate the total emission of gases from the power station, assuming the number of units on stream is known, and the % excess air utilized is known.

For the August 27th flight a total of four samples were drawn at the source with the following results:

SAMPLE	CONCENTRATION	
(1)	190	
(2)	180	Average 192 ppm
(3)	215	
(4)	185	

Basis for Calculation of Output of NO_2 from Lakeview Power Station

Lakeview Power Station give an optimum rate of coal-burning, (per unit), of 100 TPH (Tons Per Hour) which yields, theoretically, 2.8×10^6 lbs/hr of total effluent. On the 27th of August 1968, 376.3 TPH of coal were being burnt throughout the power station. This would yield 10.54×10^6 lbs per hour of total effluent, of which 192 ppm volume/volume is oxides of nitrogen, which converts eventually to Nitrogen Dioxide. The figure of 192 ppm $^V/_V$ can be converted to a $^W/_W$ value by multiplying by the ratio of the densities of NO_2 and flue gas, i.e. $\times \frac{23}{15}$, giving 294 ppm weight/weight potential NO_2 in the total flue gases.

This gives a figure of 1.55 Tons Per Hour total potential NO_2 emitted on 27/8/68.

From the actual Power Station output over the hour of the analyses, which was 12.5% up over the hourly average for the day, an extra 12.5% of coal may be assumed to have been burnt, and an extra 12.5% of potential NO_2 produced. This gives a final figure of 1.75 tons for the hour in question.

It may be said, as a confirmation of the accuracy of the effluent figures provided

by Lakeview Power Station, that a calculation of theoretical SO_2 emission yields 1335 ppm $^{v}/_{v}$, based on one coal analysis, % excess air fed to the furnaces and assuming 100 % conversion of Sulphur in the coal to SO_2. Our all-time average for ppm $^{V}/_{V}$ SO_2 is 1425 ppm.

<u>September 27/68 NO_2 Plume Profiles</u>

The "ground track" or flight lines and the plume outline are shown on the map of Figure 3.13. The purpose of this flight was to obtain remote measurements of mass flow from both above and below the plume and to compare both sets of measurements with measurements taken at the source using standard wet chemistry methods. Figure 3.14 shows the actual strip chart profiles of two traverses (including additional plume from another refinery) and Table 3.5 lists all data obtained.

Figure 3.15 illustrates in a simplified form, the profiles obtained for all passes over and under the plume.* The aircraft altitude for the overpass was 457 meters msl for all three lines and was estimated to be 30 - 40 meters above the plume at the plumes highest point i.e. at the 8,050 meter traverse. The aircraft altitude for the underpass for all lines was 138 meters msl which was about 55 meters above the lake surface. With a light (4 mph) wind, the combined plume from the refineries numerous emitting sources was quite irregular in shape and resulted in con- considerable variation on plume cross section from one pass to the next (at a given range) as shown in Figure 3.15. The irregular shape of the plume is also evident in the photograph taken of the plume and the source following the last traverse. Note also in Figure 3.15 that the plume cross section (profile area) has minimum value close to the stack and maximum value at a distance of 4,830 meters (5 miles) from the source indicating that under the conditions prevailing at the time, the build up of NO_2, that is the oxidation in the atmosphere of stack NO emissions, was largely complete in the distance of about 5,000 meters downwind or about 45 minutes after emission. The significant reduction in cross section from 4,830 meters to 8,050 meters downwind indicates that NO_2 is being lost from the plume by diffusion and/or subsequent reactions in the atmosphere. Note also from Figure 3.15 that the plume cross sections from above the plume tend to be larger than cross sections obtained from below the plume. This is to be expected since the radiation source used in the normal look-down mode is the total sky while in the look-up mode it is only a resolution element of the sky directly above the aircraft. A comparison of the look-down to look-up profiles yields a plume m factor similar in meaning to the m factor of a distributed gas layer but peculiar to the plume geometry and sky conditions which existed at the time of the measurement. Because of the "lumpy" shape of the plume considered here, good repeatibility of the measurement is demonstrated only at the 4,830 meter crossing (traverses 4,5,6, & 7). Here the overpass repeats within 25% and the underpass within 6%.

* The base of the triangle is scaled to the width of the chart profile and the area is scaled to the integrated area of the plume profile on the chart.

PLUME DATA - SEPTEMBER 27th, 1968 - OIL REFINERY

TRAVERSE NO.	TIME EST	OVER/ UNDER	PROFILE AREA (cm^2)	AVERAGE HEIGHT (cm)	VERTICAL SCALE $\frac{(ppm\text{-}m)}{cm}$	AVERAGE BURDEN (ppm-m)	PLUME X SECTION ($\frac{ppm\text{-}m^2}{x\ 10^3}$)
1	15.45	O	14.4	1.92	29.4	56.5	124
2		O	8.4	2.05	29.4	60.3	72.5
3		U	2.6	140	26.3	10.5	20
4	16.00	O	32.0	1.47	16.6	24.4	159
5		O	40.3	1.90	16.6	31.6	196
6	16.15	U	24.2	2.35	9.6	22.6	68
7		U	25.7	2.79	9.6	26.8	72
8	16.30	O	24.8	1.80	16.6	29.8	120
9	NO DATA						
10		U	30.4	3.22	9.6	30.9	85
11	16.50	U	12.8	1.58	9.6	15.2	36

Profile horizontal scale 1 cm = 293 meters

TABLE 3,5

The mass flow in both cases can be calculated as follows:

for traverses 4, 5 (over pass)

profile area = 36 cm^2 average

vert. scale = 16.6 ppm-m/cm

horiz. scale = 293 meters/cm

plume x section = 36 x 16.6 x 293 = 175 x 10^3 ppm-m^2 average

wind = 1.79 meters/sec. (4 mph)

NO_2 density = 1.95 gms/liter @ 70°F & 1 atm (single molecule)

m factor = 2.7 (1400 EST Sept 27th θz = 52° homogeneous layer

$$\text{Therefore mass flow} = 175 \times 10^3 \times \frac{1}{2.7} \times 1.79 \times 1.95 \times 10^3 \times 10^{-6}$$

$$= 226 \text{ gms/sec}$$

$$\doteq \underline{1{,}805 \text{ lb/hr}}$$

Similarly for traverses 6,7 (under-pass)

area = 25 cm^2 average

vert. scale = 9.5 ppm-m/cm

horiz. scale = 293 meters/cm

$$\text{Therefore plume x section} = 25 \times 9.5 \times 293$$

$$= 69.6 \times 10^3 \text{ ppm-m}^2 \text{ average}$$

$$\text{and mass flow} = 69.6\ 10^3 \times 1.79 \times 1.95 \times 10^3 \times 10^{-6}$$

$$= 243 \text{ gms/sec}$$

$$= \underline{1{,}940 \text{ lb/hr}}$$

Of the two results the underpass measurement should be the most accurate since uncertainties in m factor are avoided.

The actual plume m factor may be found from the ratio of plume x sections

$$\text{i.e. plume m factor} = \frac{175 \times 10^3}{69.6 \times 10^3}$$

$$= 2.51$$

This value compares very well indeed with the theoretical value of 2.7 used above. The fact that it is less than the theoretical value is to be expected since the plume width is limited and some radiation reaching the spectrometer would have passed through the plume only once.

Refinery Ground Truth

Simultaneous with the airborne measurement, wet chemistry measurement of total oxides of nitrogen were taken at the primary sources of emissions within the refinery complex.

Results are as follows:

Emitting Source	Volume flow ft^3/min	ppm $^v/_v$ NO_2	NO_2 ft^3/min
Boiler House	108,000	270	30
#1 Crude Unit Heater	52 000	80	4
CO Boiler	167,000	240	40
Remainder	230,000	80	19
		Total NO_2	93

$$\text{Total } NO_2 \text{ from refinery} \approx 93\ ft^3/min$$
$$= 2,600 \text{ liters/min}$$
$$= 76.7 \text{ gms/sec}$$
$$= 612 \text{ lb/hr}$$

DISCUSSION OF NO_2 PLUME CHASE RESULTS

Although plume measurements of Lakeview Generating Station check very closely with ground truth values, the refinery plume measurements showed a mass flow exceeding the ground truth value by a factor of three. Although the reason for the lack of closer agreement in the second case is not known at this time, the following factors are probably significant.

(1) Lakeview is well defined and well regulated source whereas the refinery in question is a multitude of sources which are quite variable and difficult to monitor.

(2) Lakeview is an isolated source whereas numerous other industries occupying the shoreline near the refinery making it difficult to discriminate between plumes. The proximity of other industrial sources is evident in Figure 3.16.

3.5 DESCENT PROFILES

The term ascent, descent or vertical profile is used herein to describe a continuous chart recording, or plot, of spectrometer output as a function of aircraft altitude. The purpose of this experiment is to test the validity of the computerized radiation transfer equations and the atmospheric model. The preferred meteorlogical and flight conditions for this experiment are as follows:

(1) A single, well defined inversion layer with a substantial concentration of pollutant uniformily distributed in the mixing layer i.e. in the layer of air between the inversion and the ground.
(2) minimal cloud cover
(3) smooth, unidirectional, low speed wind
(4) well defined identification points on the ground
(5) no low level flight restrictions
(6) adequate light

The flight procedure is to fly the aircraft along a horizontal, straight line course between two well defined points in space, first in one direction with the spectrometer looking at the sky above the aircraft and then in the opposite direction with the spectrometer looking at the ground below the aircraft. This is repeated at 2-3 thousand foot intervals from a maximum altitude of 11000 ft. to the minimum altitude consistent with flight safety.

The Lake Ontario air space again provides many of the desired features for this experiment. Prominent shoreline features make excellent identification points and dense population centers provide adequate pollution levels for all wind directions with the exception of easterlies between 060° to 120°

A total of four flights were accomplished; three NO_2 descents and one SO_2 descent. One NO_2 descent was performed over Lake Simcoe (50 miles North of Toronto) because of good meteorlogical conditions in the area and visibly dense cloud.

of pollution produced by the Toronto area and south easterly winds. Each flight is discussed in detail below.

NO_2 Descent over Lake Simcoe Sept. 17/68

Figure 3.17 shows the flight line. Figure 3.18 (a) shows the change in NO_2 channel response in volts as a function of altitude and is a plot of the total signal data column of Table 3.6. At each altitude the calibration cell was used to obtain the incremental sensitivity and scale factor which was then used to convert the change in total signal to equivalent gas burden. Note that the total signal voltage and hence the total equivalent burden is normalized to the last traverse at the lowest altitude flown in the look-up mode i.e. Run 12 of Table 3.6. The plotted data of Figures 3.18 (b) and 3.19 are therefore only relative i.e. they show only the difference in spectrometer output between the reading taken at a given altitude and the reading obtained at the last traverse.

As noted in Figure 3.17 and indicated in Figures 3.18 (a) and 3.18 (b), two stable inversion layers were observed from the aircraft. These are usually noted in flight during an initial ascent and altitude readings taken when co-altitude with the top of the haze. When the top of the haze is well defined its altitude can be judged with a reaptability of + 200 ft.

When descending through a gas layer to which the instrument is sensitive, the instrument output can be expected to fall as the total effective optical path-length (aircraft to ground to top of layer) is reduced. As can be seen in Figure 3.18 (a) and 3.18 (b) this is indeed the case, in fact there is significant fall off in signal before the upper haze layer was reached indicating that some gas was present above this level.

Referring now to the look-up mode; as the aircraft descended down through the layer,

NO_2 DESCENT DATA LAKE SIMCOE - September 17, 1968

RUN NO.	A/C ALT MSL (ft)	TIME EDT	LOOK UP/DOWN	SIGNAL OFFSET (mv) (2)	SIGNAL RDG (mv) (3)	SIGNAL TOTAL (mv) (4)	VERT SCALE ($\frac{\text{ppm-m}}{100\ \text{mv}}$)	SENSITIVITY ($\frac{\text{mv}}{\text{ppm-m}}$)	TOTAL EQUIVALENT BURDEN (ppm-m) (5)
1	11,000	16:10	U	420	590	518	65	1.54	337
2	"		D	700	140	848	66	1.51	560
3	9,000	16:20	D	700	0	708	66	1.51	467
4	"		U	700	48	755	66	1.51	498
5	7,000	16:35	U	DATA NOT GOOD					
6	5,000	16:50	D	560	10	578	47	2.13	272
7	"		U	700	0	708	47	2.13	333
8	3,000	17:05	D	280	35	323	45	2.22	145
9	"		U	280	30	318	45	2.22	143
10	1,000	17:20	D	140	42	190	37	2.70	70
11	"		U	0	34	42	37	2.70	16
12	"		U	0	-8	0	37	2.70	0

Notes:
(1) Average time of traverse
(2) Offset voltage req'd to maintain trace on chart. Relative to an assigned offse voltage of zero for run 12.
(3) Measured from zero grid line on strip chart.
(4) These values represent a change in the sum of the offset voltage and the chart reading from an assigned total signal of zero for run 12.
(5) Relative to an assigned total equivalent burden of zero for run 12.

TABLE 3.6

NO_2 DESCENT DATA - LAKE ONTARIO, OFF NIAGARA, October 2, 1968

RUN NO.	A/C ALT MSL (ft)	TIME EDT	LOOK UP/DOWN	SIGNAL OFFSET (mv) (2)	SIGNAL RDG (mv) (3)	SIGNAL TOTAL (mv) (4)	VERT SCALE $\left(\frac{\text{ppm-m}}{100\ \text{mv}}\right)$	SENSITIVITY $\left(\frac{\text{mv}}{\text{ppm-m}}\right)$	TOTAL EQUIVALENT BURDEN (ppm-m) (5)
1			U	500	200	660	45	2.22	297
2			D	500	100	560	42	2.38	235
3	9,000	1,150	U	500	240	700	47	2.13	315
4	"		D	500	140	600	38	2.62	228
5	7,000	1,220	U	500	270	730	45	2.22	328
6	"		D	500	80	540	38	2.62	205
7	5,000	1,250	U	500	170	630	40	2.50	252
8	"		D	500	40	500	40	2.50	200
9	3,000	1,320	U	0	180	140	39	2.56	54.5
10	"		D	0	40	0	39	2.56	0

Notes:
(1) Average time of traverse
(2) Offset voltage req'd to maintain trace on chart. Relative to an assigned offset voltage of zero for run 12.
(3) Measured from zero grid line on strip chart.
(4) These values represent a change in the sum of the offset voltage and the chart reading from an assigned total signal of zero for run 12.
(5) Relative to an assigned total equivalent burden of zero for run 12.

TABLE 3.7

NO_2 DESCENT DATA - LAKE O[illegible]IO OFF NIAGARA October 16, 1968

RUN NO.	A/C ALT MSL (ft)	TIME EDT	LOOK UP/DOWN	SIGNAL OFFSET (mv) (2)	SIGNAL RDG (mv) (3)	SIGNAL TOTAL (mv) (4)	VERT SCALE $\left(\frac{ppm\text{-}m}{100\ mv}\right)$	SENSITIVITY $\left(\frac{mv}{ppm\text{-}m}\right)$	TOTAL EQUIVALENT BURDEN (ppm-m) (5)
1	9,000	1,624	U	+500	500	900	21	4.75	189
2	"	1,628	U	"	600	1000	21	4.75	210
3	"	1,633	D	"	300	700	23	4.32	161
4	"	1,640	D	"	350	750	23	4.32	173
5	7,000	1,650	U	"	650	1050	21	4.75	220
6	"	1,656	D	"	300	700	21	4.75	147
7	5,000	1,704	U	"	600	1000	19	5.25	190
8	"	1,710	D	"	225	625	19	5.25	119
9	3,000	1,718	U	"	525	925	20	5.0	185
10	"	1,724	D	"	100	500	19	5.25	95
11	1,000	1,732	U	"	375	775	20	5.0	155
12	"	1,738	D	0	190	90	21	4.75	19
13	500	1,743	U	0	400	300	19	5.25	57
14	"	1,749	U	0	425	325	19	5.25	62
15	"	1,754	D	0	100	0	21	4.75	0
16	"	1,759	D	0	150	50	21	4.75	10

Notes:
(1) Average time of traverse
(2) Offset voltage req'd to maintain trace on chart. Relative to an assigned offset voltage of zero for run 12.
(3) Measured from zero grid line on strip chart.
(4) These values represent a change in the sum of the offset voltage and the chart reading from an assigned total signal of zero for run 12.
(5) Relative to an assigned total equivalent burden of zero for run 12.

TABLE 3.8

SO_2 DESCENT DATA - LAKE ONTARIO OFF HAMILTON. November 4. 1968

RUN NO.	A/C ALT MSL (ft)	TIME EDT (1)	LOOK UP/DOWN	SIGNAL OFFSET (mv) (2)	SIGNAL RDG (mv) (3)	SIGNAL TOTAL (mv) (4)	VERT SCALE $\left(\frac{\text{ppm-m}}{100\ \text{mv}}\right)$	SENSITIVITY $\left(\frac{\text{mv}}{\text{ppm-m}}\right)$	TOTAL EQUIVALENT BURDEN (ppm-m) (4)
1	9000	1220	U	0	225	1025	35	2.85	359
2	"		U	0	260	1060	39	2.56	413
3	"		D	0	720	1520	31	3.22	471
4	"		D	0	675	1475	31	3.22	457
5	7000	1235	D	0	600	1400	28	3.56	392
6	"		U	500	150	450	44	2.27	202
7	5000	1245	D	0	400	1200	39	2.56	468
8	"		U	500	100	400	39	2.56	156
9	"		D	0	440	1240	39	2.56	484
10	3000	1255	U	700	250	350	30.5	3.27	107
11	"		D	0	500	1300	31	3.22	403
12	1000	1315	U	700	400	500	34.5	2.90	173
13	"		D	0	800	1600	22	4.52	352
14	"		U	700	350	450	31	3.22	140
15	"		D	0	600	1400	37.5	2.66	525
16	9000	1335	U	400	300	700	34	2.95	238
17	"		D	0	400	1200	37.5	2.66	450

Notes:
(1) Average time of traverse
(2) Offset voltage req'd to maintain trace on chart
(3) Measured from zero grid line on strip chart
(4) These values are not absolute and represent only a change in response as a function of altitude.

TABLE 3.9

one would expect to see a monotonic increase in total gas within the view of the instrument. Referring to Figures 3.18 (a) and 3.18 (b) however, it can be seen that an increase was recorded only down to the highest haze layer and descending further produced an apparent reduction in the total number of molecules seen by the instrument. Since this is obviously an impossibility, additional flights were made for NO_2 on Oct. 2 and Oct. 16, 1968. As shown in Figures 3.21 and 3.24, the look-up profiles consistently show little change or a slight increase in look-up signal down to the inversion layer and then very definite negative tendencies below this level. This behaviour can be explained in terms of instrument mechanization. As shown in Appendix I, the spectrometer response not only to the absorption characteristics of the gas it is programmed for, but also to changes in spectral distribution of the radiation source. In the aircraft of course the look-up radiation source is the sky whose spectral characteristics depend on both sun angle and the scattering characteristics of the atmosphere. For a given sun angle, scattering characteristics depend on particle size and number distribution which are quite variable in the lower levels of the atmosphere and particularly so at the top of a haze layer. In the foregoing Figures the negative going NO_2 channel signal is the net result of two responses, namely a positive going NO_2 absorption signal and a negative going spectral gradient signal, of which the latter predominates. Above the haze layers the response is predominantly NO_2 absorption. Figure 3.19 shows graphs of the photomultiplier (PM) voltage and sensor sensitivity plotted against altitude. The curve of PM voltage which is an inverse function of light level shows a significant low point right at the strong inversion altitude of 5,000 ft. msl. This means that the light intensity looking up into the haze layer from immediately below it was higher than at any other point in the descent. This would be due to enhanced long wavelength contributions from large particle and aerosol scatterers in the haze layer.

The change in instrument sensitivity shows a definite tendency to increase below the inversion in the look-up mode. This is due to a general levelling of the spectral distribution due again to enhancement of the long wavelength contributions.

It is worth noting here that the gradient error evident in the look-up data will be present to a much lesser extent in the look-down mode because the radiation source includes direct radiation from the sun (via the earths surface) and therefore the affect of shifts in energy distribution in backscatter from haze will be less pronounced.

<u>NO_2 Descent over Lake Ontario October 2/68.</u>

This flight was discontinued after descending to the 3,000 ft. level because of weather. The data however is quite good and confirms the results of the Lake Simcoe flight as mentioned earlier.

<u>NO_2 Descent over Lake Ontario October 16/68.</u>

This flight was carried out under extremely good conditions. The results are essentially the same as for previous flights with the exception of a low haze layer at about 700 ft. msl. A photograph of this low layer is shown in Figure 3.26. Unfortunately the aircraft was not really co-altitude with the top of this haze and the interface is not as clear as the visual observation. A dashed line approximates the haze top.

SO_2 Descent Over Lake Ontario - November 4, 1968

Figure 3.27 shows the flight line and as indicated by the wind arrows, the descent was made through pollution carried by a north east wind. The spectrometer millivolt output is shown plotted against a/c altitude in Figure 3.28 and the same output in terms of ppm-meters is presented in Figure 3.29. Note in Figure 3.29 that the change in apparent gas burden changes sign several times during the descent indicating that the gradient component of signal is at least as large as the true SO_2 signal and can be positive or negative relative to the SO_2 absorption signal.

The effect of changes in spectral gradient or instrument sensitivity is evident in Figure 3.30. Although the number of data points on any one profile is rather limited, there is nevertheless a strong correlation between the locations of the points of inflection on the look-down sensitivity curve and the layers of stable air in the atmosphere. During the descent, temperature readings of ambient air were taken using the aircraft thermometer, which has a readout resolution of 1°C. These data are shown plotted in the lower curve with the stratified layers of stable air shown by shaded areas. Stable layers of air are indicated by temperature gradients less than the dry adiabatic lapse rate i.e. less than a fall of about 1°C for every 500 ft. increase in altitude.

3.7 GENERAL COMMENTS ON FLIGHT RESULTS

The foregoing flight results including NAPCA Chattanooga work, reference (1) confirm the results of the previous contract NAS9-72 42 in terms of feasibility of the remote detection of SO_2 and also clearly establish the feasibility of remote detection of atmospheric NO_2 and I_2. Quantitatively, more ground truth data has been gathered for NO_2 than for SO_2 and good ground truth comparisons for I_2 have yet to be accomplished. The most useful and most accurate ground truth data to date, in so far as proving the remote sensor is concerned, have been the NO/NO_2 stack measurements. In general the comparisons of airborne - ground level measurements of NO_2 in Los Angeles and Toronto plus preliminary results of Chattanooga (NAPCA is currently finalizing the Chattanooga data analysis) are so encouraging that no changes to the NO_2 atmospheric model are contemplated, at least until the results of more precise experiments are available. The SO_2 airborne-ground level comparisons on the other hand consistently indicate that airborne results tend to be higher than the actual. Apart from the spectral gradient problems discussed below, a contributing factor to the apparent error may lie in the values assigned to the SO_2 absorption coefficients used in the SO_2 atmospheric model. Theoretical work is presently underway to obtain more precise values and these findings will then be used, along with more accurate comparisons with ground emissions, to refine the model.

The generation of accurate Iodine ground truth data promises to be perhaps the easiest gas to handle so far. It appears quite feasible to set up an experimental I_2 vapor generator with sufficient strength to serve as an effective calibrated source. For example, a 50 ppm-meter response of 5 second duration could be obtained from a plume with a source strength of 35 gms/sec (50 lb/minute) in a 5 meter/sec (11 mph) wind. Such a facility could comprise a battery of truck-mounted hot air blowers exhausting into the atmosphere through high capacity I_2 evaporators. A mobile test site of this kind could be readily set up, for example on the shores of Lake Ontario and the plume "chased" in the conventional manner.

Perhaps the most significant feature of the test results is the magnitude of the error in the measurement caused by changes in spectral distribution. Insufficient data were available from the original feasibility flights to reveal this error and in fact it was not until after the final series of equipment modifications (following the Los Angeles work in May of 1968) that this type of error became clearly identifiable. This was subsequently confirmed by the theoretical treatment given in Appendix I and the NO_2 and SO_2 descent experiments. It is important to note here that this type of error has not had a substantial effect on relative measurements of gas clouds in the look-down mode. In other words, in plume chasing experiments where the plume contribution is measured relative to the background pollution, e.g. the Toronto plume chases, the apparent accuracy of the measurement has been most encouraging. It is when attempting to measure the absolute level of pollution in the atmosphere using the sky as a zero reference that the spectral gradient error has a significant effect on the accuracy of the result. Furthermore this type of error is largest in the ultra-violet (SO_2) mode and least in the blue=visible (NO_2) mode. The unexpectedly high SO_2 levels found in the Washington D.C. and Los Angeles surveys may be due in part to the presence of spectral gradient errors in the measurement. There is also good reason to believe that a large part of the background fluctuations present in the synoptic profiles of all three gases is due to spectral gradient noise components. These will be induced not only by variable atmospheric scattering but also by the spectral characteristics of the terrain. As shown by Figures 3.7 and 3.8, the nature of the terrain has little affect on background noise in the SO_2 and NO_2 modes but is quite pronounced in the I_2 mode as shown in Figure 3.4. This is so because the wavelength dependency of the reflectance properties of most terrain materials in the middle near ultra-violet is not strong as shown in reference (3) but is quite pronounced in the visible as shown in reference (4). The relatively high background noise level in the SO_2 mode then can be attributed mainly to a fluctuating gradient of the ground-reflected radiation caused by atmospheric effects plus, no doubt, a noise contribution from the SO_2 concentration pathlength product.

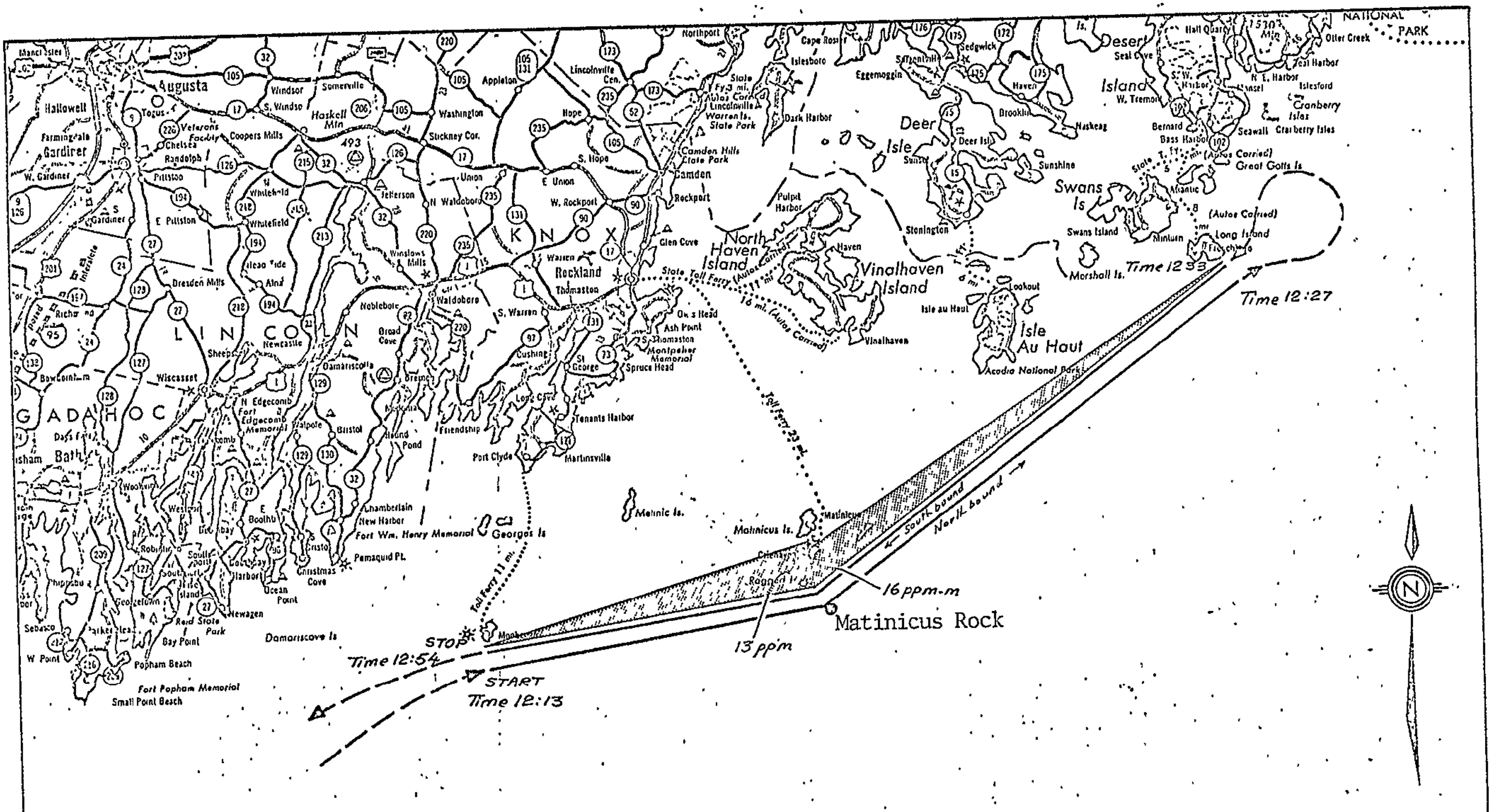
The NO_2 mode of operation appears to be the least affected by gradient errors due to either terrain or atmospheric effects.

Unwanted scattered radiation from the pollution layers in the atmosphere may not only modify the spectral distribution of radiation reaching the instrument but it may also enhance or dilute the spectral signature. The presence of backscattered radiation from the pollution layer is evident in the NO_2 descents of Figures 3.19, 3.22 and 3.25 and in the SO_2 descent of Figures 3.30. Since the sensor AGC system maintains a constant output level from the photomultiplier by automatically adjusting the PM tube voltage, an increase in voltage indicates a reduction of radiation received. Note that in the look-down mode, as the aircraft descended, there was little change in PM voltage until passing through the haze layers, after which there was a gradual but steady increase, i.e. a gradual decrease in total radiation received within the spectral bandwidth. This indicates that back scattered radiation was coming from particles fairly uniformily distributed in the layer, although Figure 3.25 indicates that a particularly dense layer of scatterers occured below the lowest inversion at 700 ft.

In the normal look-down mode, the effect of backscattered radiation from aerosol and particulate matter in the atmosphere on the accuracy of the measurement will depend on the spatial distribution or location of the aerosol particles relative to the gas. If completely above the aerosol then the gas signature will not be affected and if it is completely below the aerosol then the effect of dilution will be maximum. Undoubtedly in the actual case the answer lies somewhere between these two extremes.

Techniques are now being considered which will enable the aerosol backscattering effect to be estimated and allowed for in computing gas burdens in the atmosphere. The basis of one approach is the aforementioned fact that most terrain materials have relatively flat reflectance properties in the ultra-violet whereas back-

Scattered radiation from aerosols in the atmosphere is highly wavelength dependent. Therefore by monitoring the radiation coming back from both the earth's surface and the atmosphere at two or more selected wavelengths, it is hoped to estimate the aerosol backscatter component and apply this as a dilution correction factor to the instrument reading.



I$_2$ SEARCH

Coast of Maine, U.S.A.

Aug 11th 1968

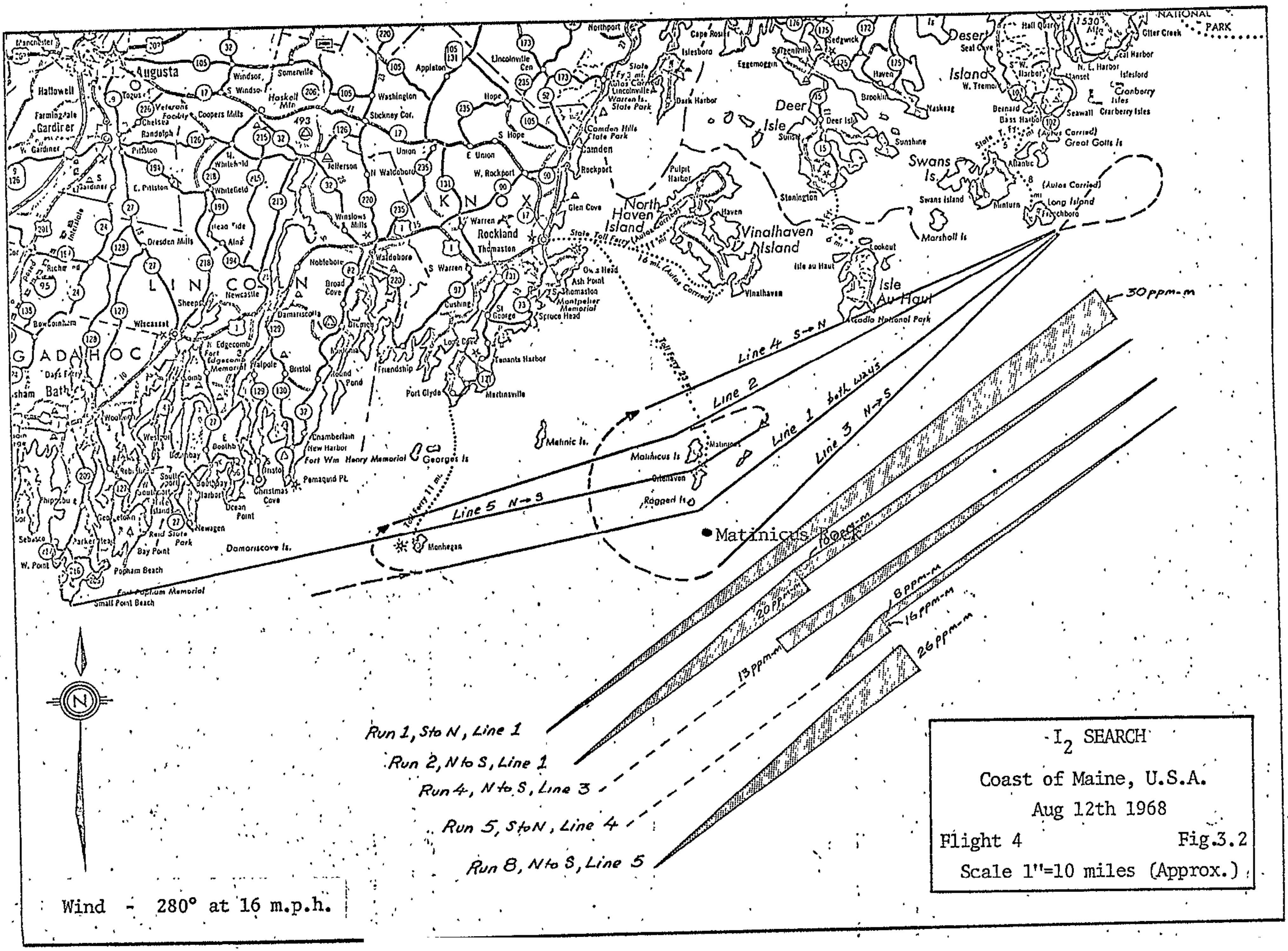
Flight 3 Figure 3.1

Scale 1"=10 miles (Approx.)

Wind - N.W. Very light

Northbound - Sidelook at 3,500 ft. Alt.

Southbound - Sidelook at 2,500 ft. Alt.



Wind - 280° at 16 m.p.h.

I_2 SEARCH

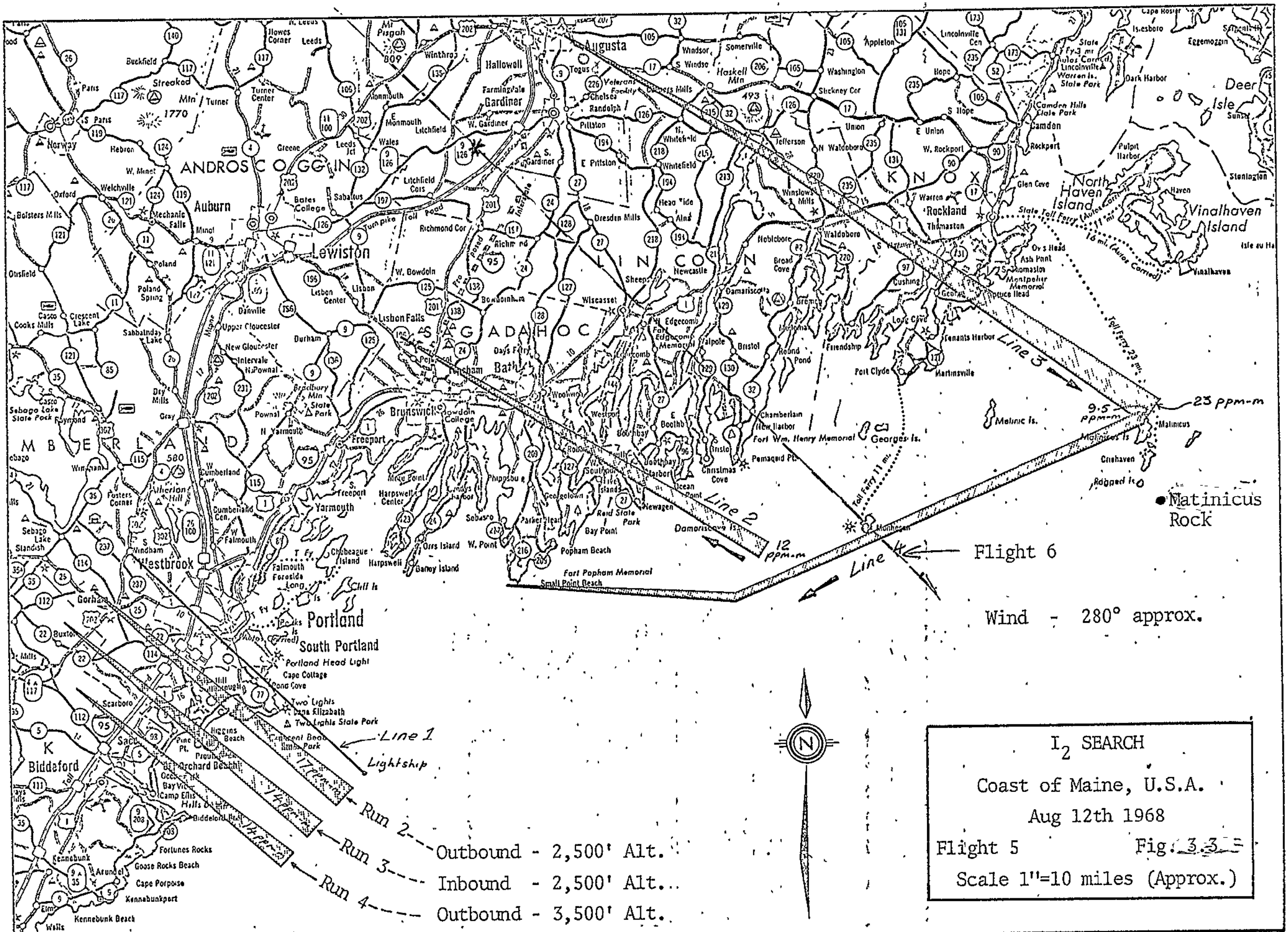
Coast of Maine, U.S.A.

Aug 12th 1968

Flight 4

Fig.3.2

Scale 1"=10 miles (Approx.)



Line 1
Lightship
Line 2
12 ppm-m
Line 3
9.5 ppm-m
23 ppm-m
Line 4
Flight 6
Wind - 280° approx.
Matinicus Rock
Run 2 - Outbound - 2,500' Alt.
Run 3 - Inbound - 2,500' Alt.
Run 4 - Outbound - 3,500' Alt.
I_2 SEARCH
Coast of Maine, U.S.A.
Aug 12th 1968
Flight 5
Fig. 3-3
Scale 1"=10 miles (Approx.)
Augusta
Lewiston
Auburn
Brunswick
Bath
Portland
South Portland
Biddeford
Rockland
Monhegan
ANDROSCOGGIN
SAGADAHOC
LINCOLN
KNOX

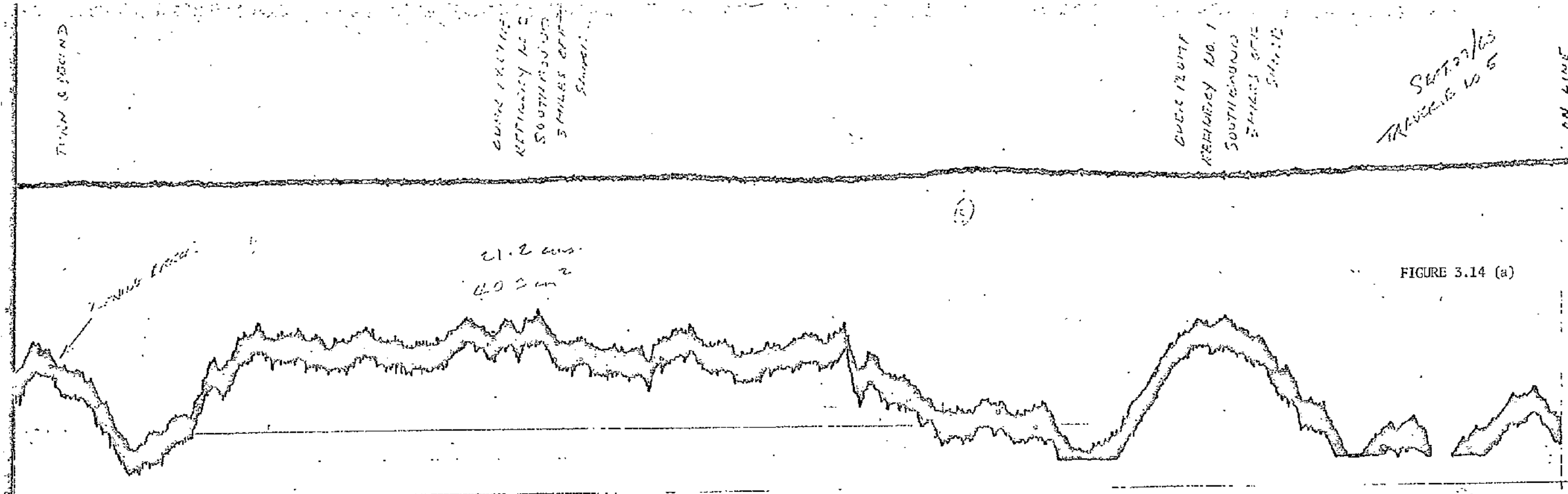


FIGURE 3.14 (a)

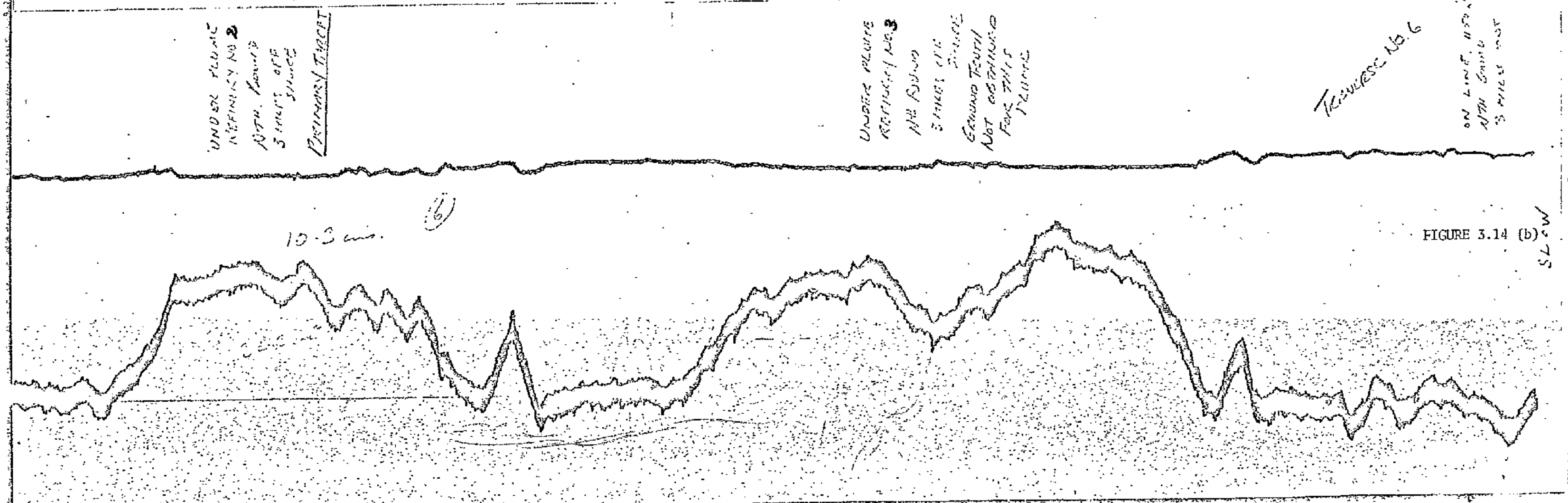
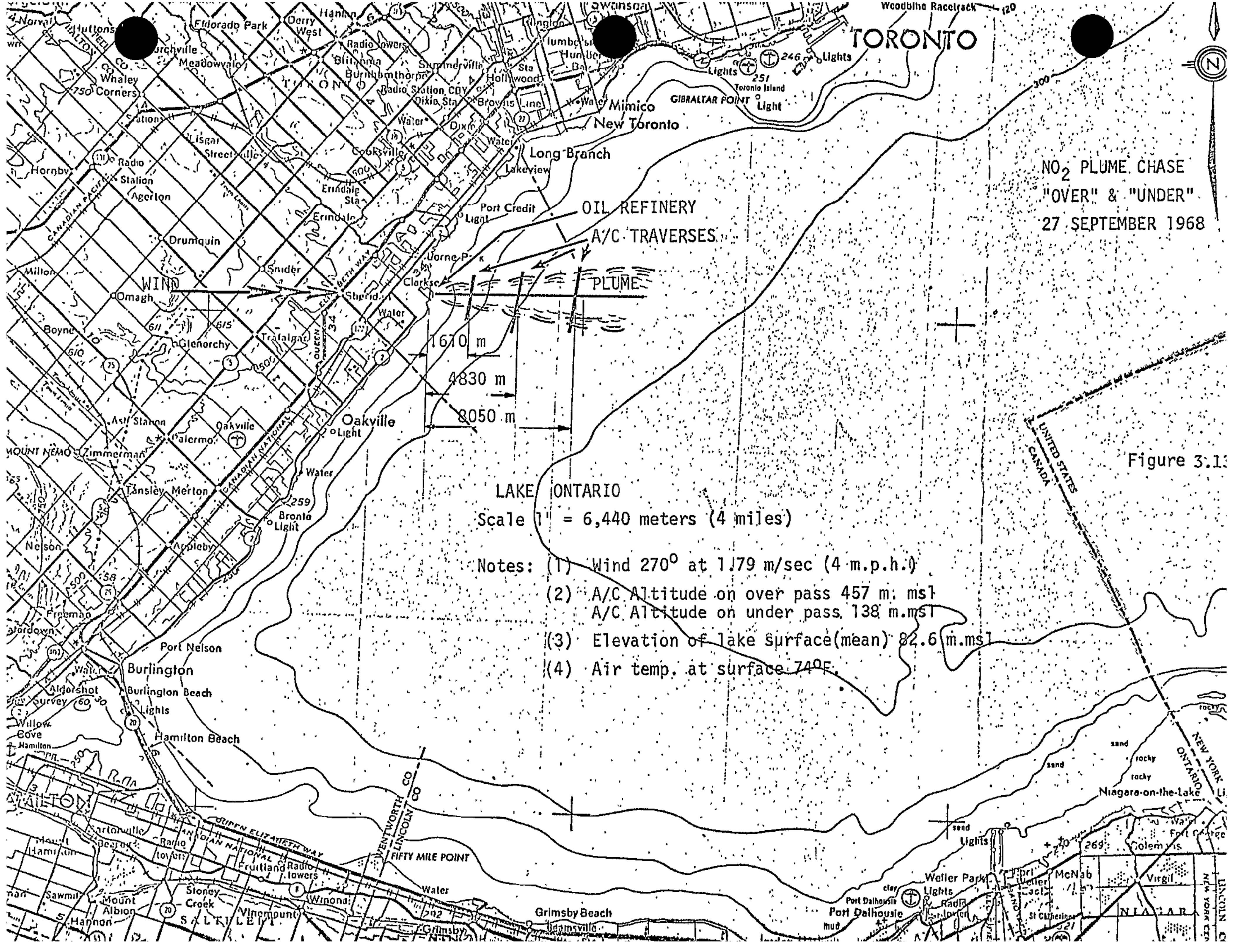


FIGURE 3.14 (b)



NO$_2$ PLUME CHASE
"OVER" & "UNDER"
27 SEPTEMBER 1968
TORONTO
OIL REFINERY
A/C TRAVERSES
WIND
PLUME
1610 m
4830 m
8050 m
LAKE ONTARIO
Scale 1" = 6,440 meters (4 miles)
Notes: (1) Wind 270° at 1.79 m/sec (4 m.p.h.)
(2) A/C Altitude on over pass 457 m. msl
A/C Altitude on under pass 138 m.msl
(3) Elevation of lake surface(mean) 82.6 m.msl
(4) Air temp. at surface 74°F.
Mimico
New Toronto
Long Branch
Port Credit
Oakville
Bronte
Burlington
Hamilton Beach
Port Nelson
Grimsby Beach
Niagara-on-the-Lake
Port Dalhousie
FIFTY MILE POINT
UNITED STATES
CANADA
NEW YORK
ONTARIO

Figure 3.1

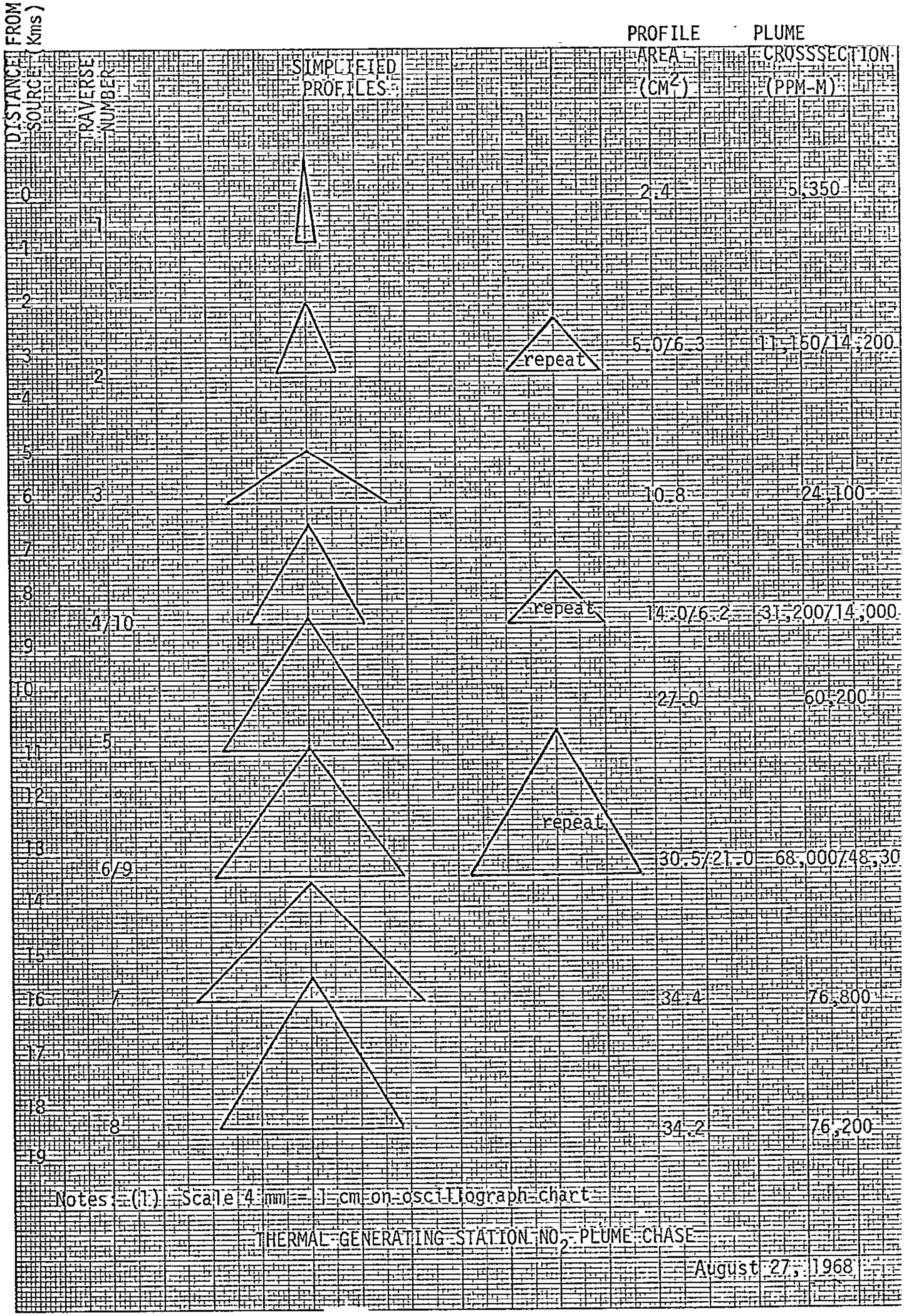

DISTANCE FROM SOURCE (Kms)
TRAVERSE NUMBER
SIMPLIFIED PROFILES
PROFILE AREA (CM²)
PLUME CROSSSECTION (PPM-M)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
1
2.4
5,350
2
repeat
5.0/6.3
11,160/14,200
3
10.8
24,100
4/10
repeat
14.0/6.2
31,200/14,000
27.0
60,200
5
repeat
6/9
30.5/21.0
68,000/48,30
7
34.4
76,800
8
34.2
76,200
Notes: (1) Scale 4 mm = 1 cm on oscillograph chart
THERMAL GENERATING STATION NO2 PLUME CHASE
August 27, 1968

Figure 3.12

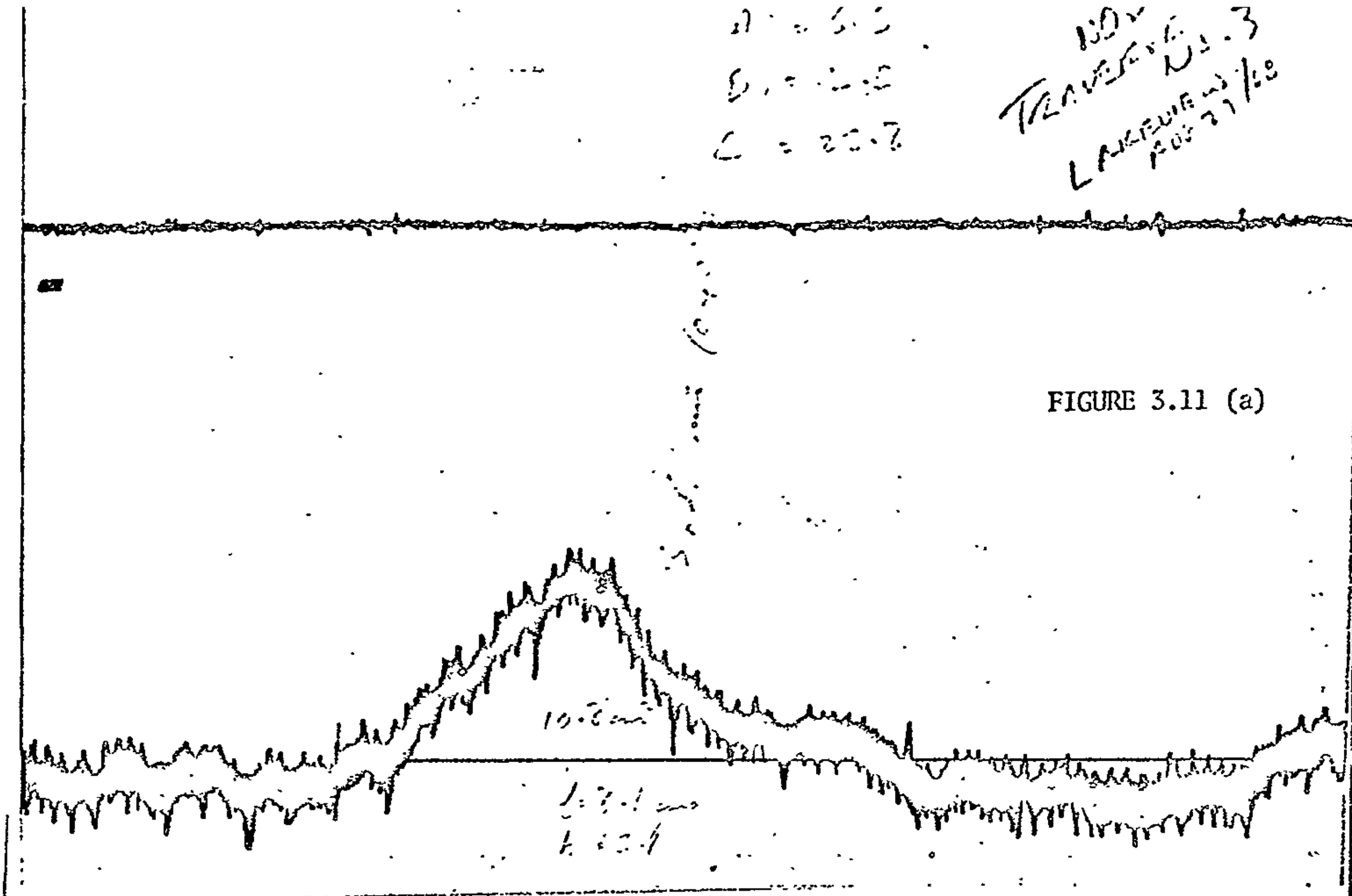


FIGURE 3.11 (a)

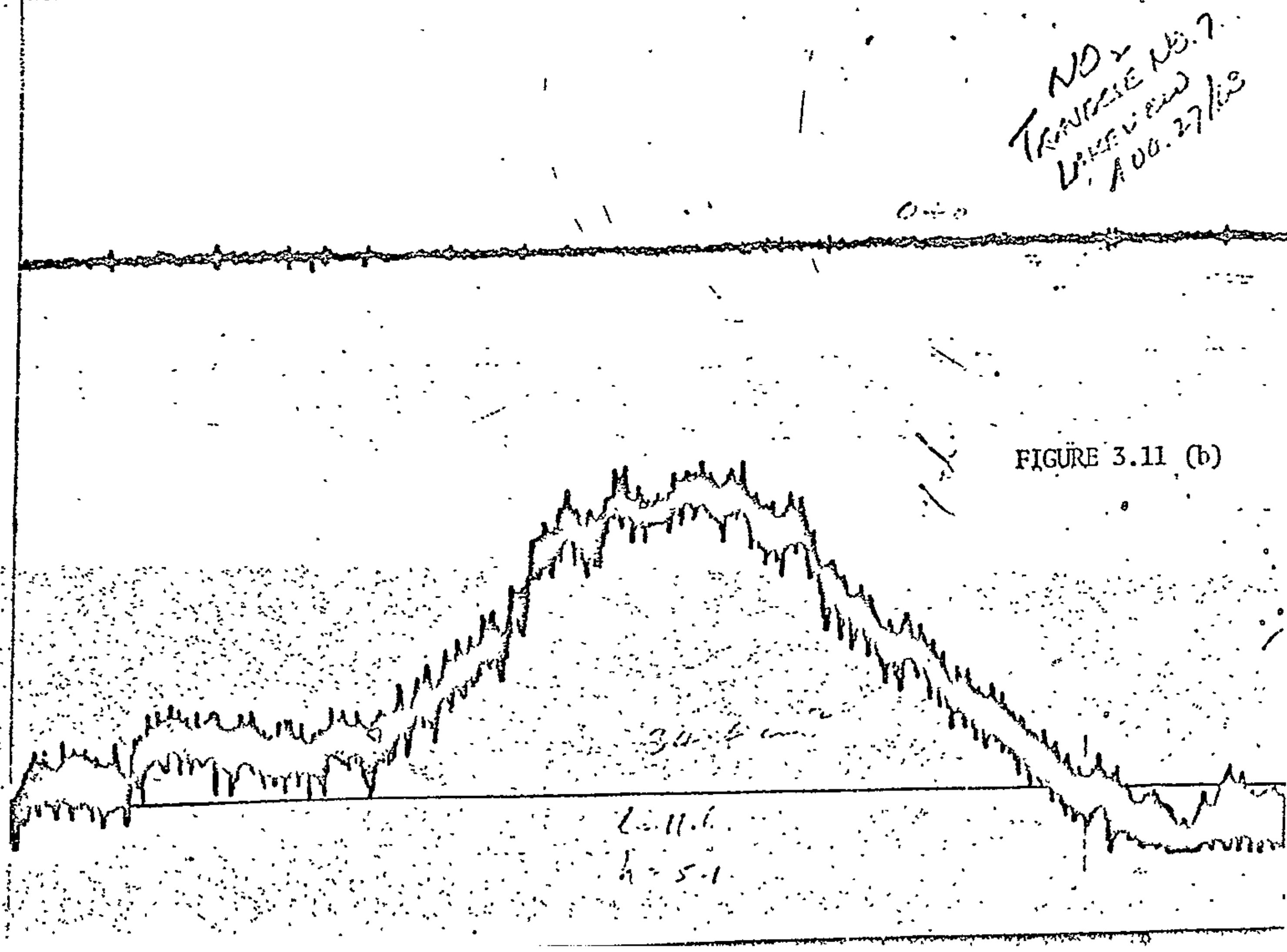
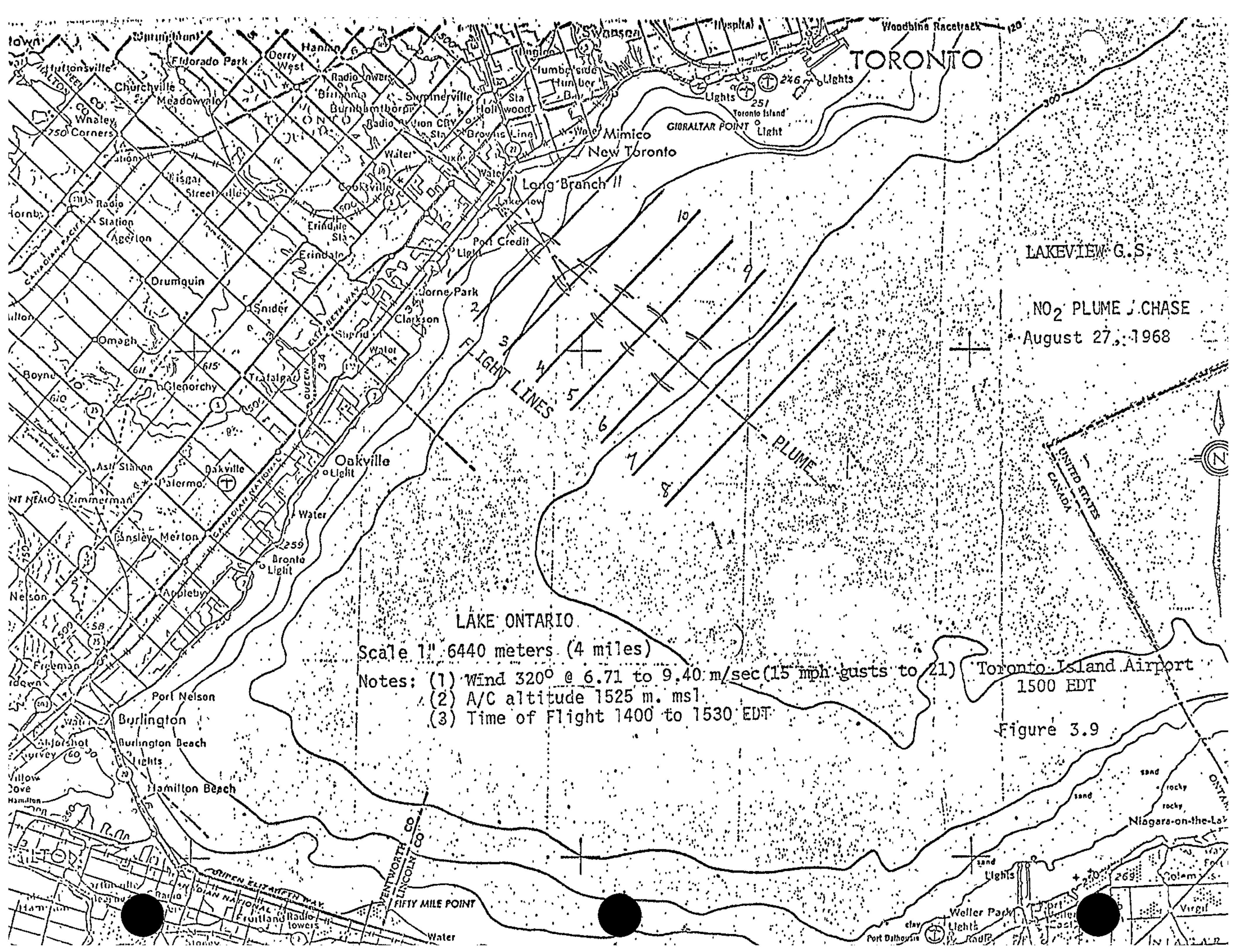


FIGURE 3.11 (b)

ONTARIO HYDRO

LAKEVIEW GENERATING STATION
FROM ABOUT 5,000 FT.

FIGURE 3.10


TORONTO
LAKEVIEW G.S.
NO_2 PLUME CHASE
August 27, 1968
FLIGHT LINES
PLUME
LAKE ONTARIO
Scale 1" 6440 meters (4 miles)
Notes: (1) Wind 320° @ 6.71 to 9.40 m/sec (15 mph gusts to 21)
(2) A/C altitude 1525 m. msl
(3) Time of Flight 1400 to 1530 EDT
Toronto Island Airport
1500 EDT
Mimico
New Toronto
Long Branch
Port Credit
Clarkson
Oakville
Burlington
Hamilton Beach
UNITED STATES
CANADA
Niagara-on-the-Lake
FIFTY MILE POINT
Figure 3.9

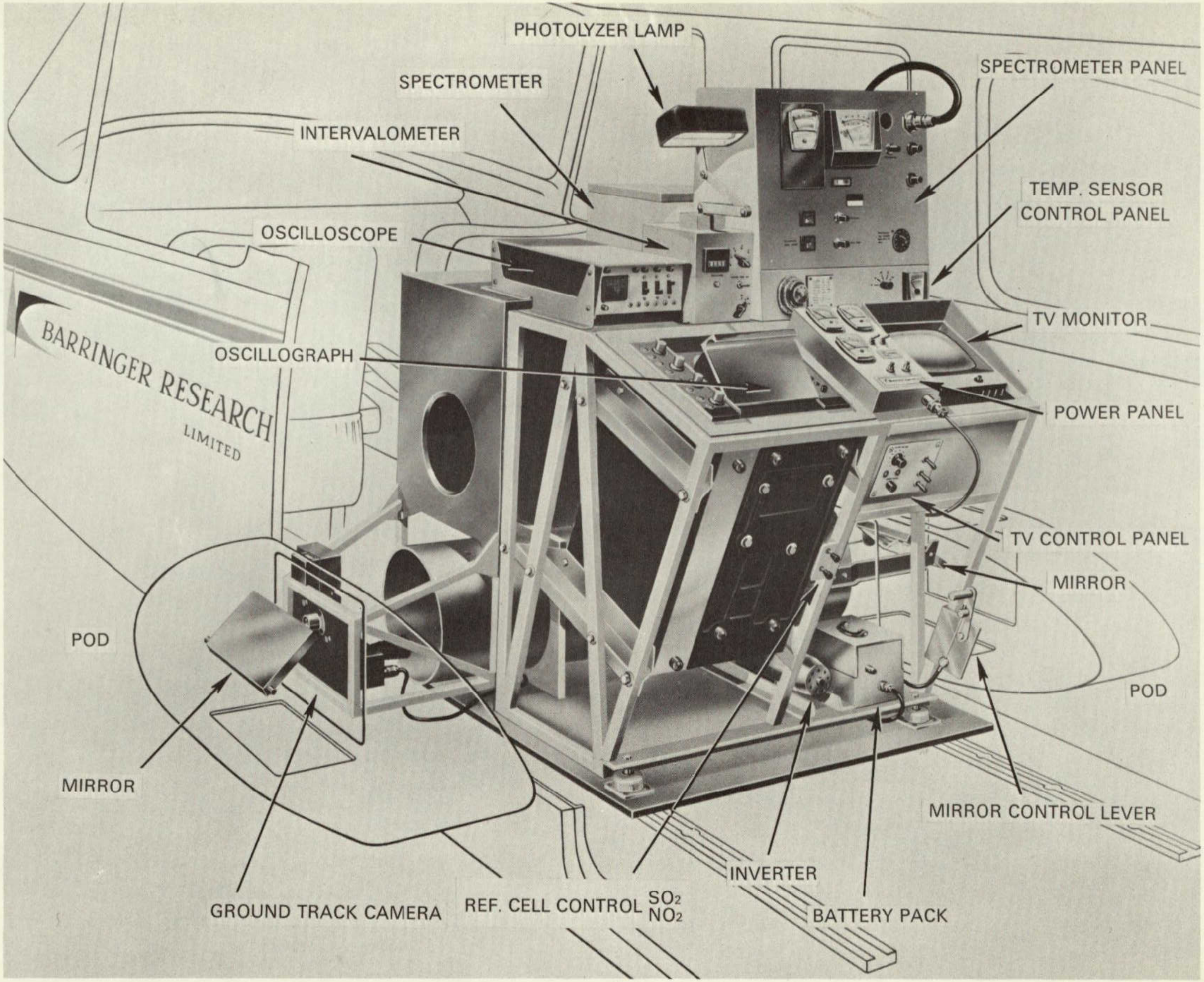
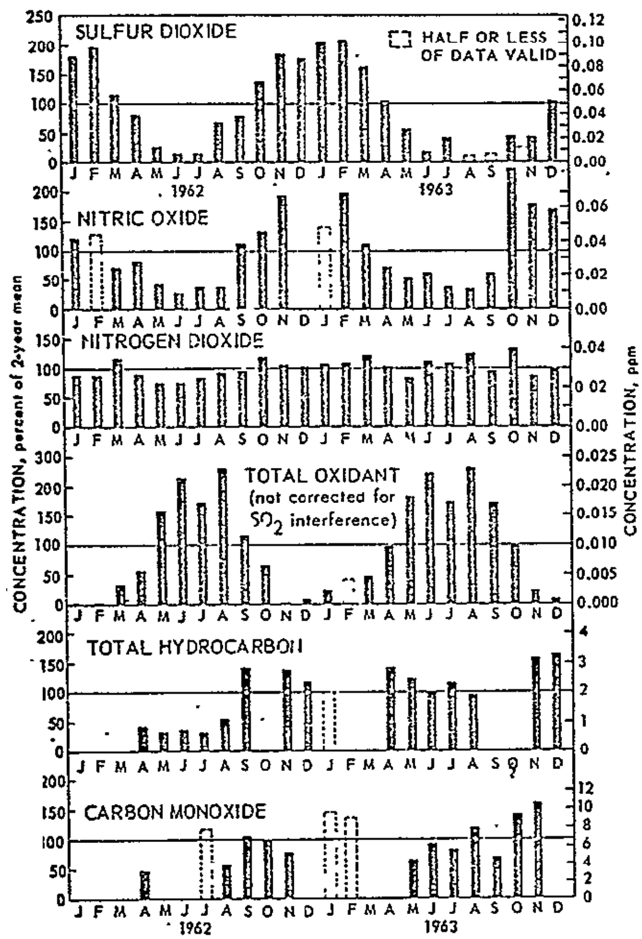

PHOTOLYZER LAMP
SPECTROMETER
SPECTROMETER PANEL
INTERVALOMETER
TEMP. SENSOR
CONTROL PANEL
OSCILLOSCOPE
BARRINGER RESEARCH
LIMITED
TV MONITOR
OSCILLOGRAPH
POWER PANEL
TV CONTROL PANEL
MIRROR
POD
POD
MIRROR
MIRROR CONTROL LEVER
INVERTER
GROUND TRACK CAMERA
REF. CELL CONTROL SO_2 NO_2
BATTERY PACK

FIGURE 1.2



Seasonal variation of gaseous pollutant levels for Washington

FIGURE 5-3